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POLYVINYL ALCOHOL SPINNING SOLUTIONS AND FIBERS PRODUCED THEREFROM

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This invention relates to the production of polyvinyl alcohol fibers of improved characteristics and is more particularly concerned with producing polyvinyl alcohol fibers of good dyeability and whiteness.

Commercial polyvinyl alcohol fibers, such as the so-called "Vinylon," which are produced by spinning an aqueous solution of polyvinyl alcohol and then subjecting the fibers to heat treatment and acetalization, such as formalization, do not have as good dyeability as is generally desired so that various methods have heretofore been proposed in an effort to remove this limitation. Thus, it is known that the dyeability of Vinylon can be improved by using a mixed spinning solution composed of polyvinyl alcohol and water-soluble, nitrogen-containing polyvinyl alcohol derivatives, such as partially-aminoacetalized polyvinyl alcohol, partially cyanoethylated polyvinyl alcohol, and the like. The fibers thus obtained, however, have the drawback that they tend to yellow when they are subjected to heat treatment and the improvement in dyeability is generally insufficient. The spinning of a mixed spinning solution containing polyvinyl alcohol in admixture with polyvinyl alcohol derivatives which do not contain nitrogen, such as water-soluble, partially-saponified polyvinyl acetate, water-soluble, partially formalized polyvinyl alcohol, has also been proposed, but in this case the improvement in dyeability is again not sufficient, and, more particularly, such Vinylon subjected to acetalization with a higher aldehyde, such as benzaldehyde, in order to improve low resilience, which is one of the drawbacks of Vinylon, has considerably poorer dyeability in comparison with formalized Vinylon, so that it has been difficult to manufacture Vinylon which has both excellent resilience and dyeability.

It is thus an object of this invention to provide polyvinyl alcohol fibers exhibiting excellent dyeability and whiteness, in combination with good water resistance, heat resistance and good mechanical properties, such as resilience.

In accordance with the invention, a mixed spinning solution composed of polyvinyl alcohol and a water-soluble polyvinyl alcohol derivative containing 0.1 to 6% by weight of nitrogen derived from urea and obtained by the reaction of polyvinyl alcohol with urea, preferably in combination with a water-soluble saccharide or a water-soluble saccharide deriverative, is used to spin fibers and the resultant fibers are subjected to heat treatment and to chemical treatment, such as acetalization.

After many experiments and studies, we have found that polyvinyl alcohol fibers having excellent dyeability can be produced by using a spinning solution composed of a mixture of a water-soluble saccharide of a water-soluble saccharide derivative, and polyvinyl alcohol. However, the fibers so produced, when acetalized with higher aldehydes, such as benzaldehyde, have a somewhat poorer dyeability when compared with formalized Vinylon fibers. Our continued investigations to solve this problem have led to the discovery that fibers having excellent dyeability can be obtained not only in the case of formalization but also in the case of benzalization if the fibers are spun from a mixed spinning solution composed of polyvinyl alcohol and a polyvinyl alcohol derivative containing 0.1 to 6% of nitrogen (believed to exist primarily as vinyl carbamate units) derived from urea and obtained by the reaction of polyvinyl alcohol and urea. In the case of such fibers, yellowing due to heat treatment is much reduced, in comparison with fibers formed from polyvinyl alcohol alone, and indeed, there is substantially no discoloration, and substantially white fibers are readily obtained, in contrast to known procedures using nitrogen-containing polyvinyl alcohol derivatives. In addition, greatly improved dyeability can be obtained, both in the case of formalization and in the case of benzalization, when the mixed spinning solution composed of polyvinyl alcohol and the reaction product of polyvinyl alcohol and urea also contains a water-soluble saccharide or a water-soluble saccharide derivative.

Other objects and features of the invention will be apparent from the following detailed description of the invention, including several practical examples and comparisons to illustrate its characteristics.

In Table I, Samples A and B are ordinary Vinylon obtained by wet-spinning in conventional manner a conventional wet-spinning aqueous solution of polyvinyl alcohol having a degree of polymerization of 1,700, and subjecting the resultant fibers to heat treatment (235° C., 1 min.), followed by formalization (Sample A) in an aqueous solution containing 5% of formaldehyde, 15% of sulphuric acid and 15% of sodium sulphate, at 70° C., for 1 hr., or benzalization (Sample B) in an aqueous solution containing 1.7% of benzaldehyde, 10% of sulphuric acid, and 40% of methanol, at 60° C., for 1 hr. Sample C was produced by the method of the invention using a mixed aqueous solution of the same polymer content as in Samples A and B but the polymer component being composed of 70% of polyvinyl alcohol and 30% of a polyvinyl alcohol-urea reaction product containing 1.2% by weight of nitrogen obtained by adding 10% of urea to a partially-saponified polyvinyl acetate containing 98 mol percent of vinyl alcohol and 2 mol percent of vinyl acetate and heating the mixture to 200° C. for 3 minutes. The fibers were produced from this spinning solution and subsequently treated by following the same procedure used in producing Sample A.

Sample D was produced by the method of the invention but the fibers were subjected to benzalization instead of formalization, using the procedure followed in manufacturing Sample C. Sample E consists of fibers obtained by using a spinning solution in accordance with the invention and containing a polyvinyl alcohol-urea reaction product containing 2.3% of nitrogen, the procedure used in producing Sample D being followed. Samples F and G are composed of fibers obtained by using a mixed solution consisting of a mixture of 10% and 20% of soluble starch, respectively, in a conventional aqueous solution of polyvinyl alcohol, and Samples H and I are composed of formalized and benzalized fibers, respectively, obtained by using an aqueous solution of polyvinyl alcohol combined with the reaction product of polyvinyl alcohol and urea, in accordance with the invention, and also containing soluble starch in the spinning solution. Sample J is composed of fibers obtained by using polyvinyl alcohol acetalized with β-cyclohexylaminobutyraldehyde, instead of the polyvinyl alcohol-urea reaction product, in the procedure used in producing Sample C.

In the following table, polyvinyl alcohol is abbreviated as PVA.

TABLE I

Sample	Blended polymer	Yellowing after heat treatment	Acetalization	Shrinkage in boiling water (percent)	Tenacity (g./d.)	Elastic recovery at 3% elongation (percent)	Dye-absorption [1] (mg./g. fiber)	Depth of color [2]
A		Pale yellow	Formalization	4	4.3	47	4	[3] (3)
B		do	Benzalization	6	3.8	70	1	[3] (1)
C	PVA-urea reaction product (N 1.2%) 30%.	White	Formalization	4	3.8	53	18	11
D	do	do	Benzalization	7	3.5	71	14	10
E	(N 2.3%) 30%	do	do	8	3.4	74	16	10
F	Starch 10%	Pale yellow	do	6	3.8	70	3	[3] (1)
G	Starch 20%	do	do	6	3.5	70	6	[3] (4)
H	PVA-urea reaction product (N 1.1%) 15%, starch 10%.	White	Formalization	5	3.9	50	19	12
I	do	do	Benzalization	7	3.5	72	14	12
J	Aminoacetalized PVA (N 1.2%) 30%.	Yellow	do	9	3.0	71	6	6

[1] Congo Red (C.I. Direct Red 28) 2%, 90° C., 2 hours.
[2] K/S value at 10 mg./g. dye-absorption.
$K/S=(1-R\infty)^2/2R\infty$.
R:Reflection at 520 mμ wave length.
[3] Extrapolated from dye-absorption—K/S relation.

As will be seen from the foregoing table, Sample C of the invention has the same hot water resistance and tenacity as ordinary Vinylon A, but it has considerably improved dyeability and a very high dye-absorption, and the depth of color is very high when compared at the same dye-absorption. It is believed that this advantageous result is due to the fact that, according to the method of the invention, the cross-section of the fibers is homogeneous and their transparency has increased.

The dyeability of the benzalized Vinylon D and E is nearly the same as that of formalized Vinylon C, and better than that of Sample J using the known aminoacetalized polyvinyl alcohol. Sample J is poorer in whiteness in comparison with ordinary Vinylons A and B, and discolors upon heat treatment. Samples C, D and E of the invention are pure white and have an improved whiteness in comparison with ordinary Vinylons A and B. The benzalized Vinylon of the invention has an excellent resilience, not less than that of Sample B. Samples H and I obtained by mixing the polyvinyl alcohol-urea reaction product and starch with polyvinyl alcohol both have much better dyeability and better whiteness than Samples F and G which were obtained by using only starch in combination with polyvinyl alcohol, and their dyeability is better than that of Samples C, D and E.

The polyvinyl alcohol suitable for use in accordance with the present invention is known polyvinyl alcohol and includes polymers composed principally of the vinyl alcohol radical. Polyvinyl alcohol is a polymer containing hydroxyl groups and corresponding to the formula:

$$(-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}})_n$$

wherein n is an integer which can vary within wide limits, as is well-known in the art. Polyvinyl alcohol can be produced from the corresponding polyvinyl ester, e.g., polyvinyl acetate, by alkaline or acid saponification or re-esterification, i.e., alcoholysis, in accordance with the following equation:

$$[-CH_2-\underset{\displaystyle OCOR}{\underset{|}{CH}}-]_n \xrightarrow[R'OH]{H_2O \text{ or}} [-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-]_n + n\text{HOCOR or } n\text{R'OCR}$$

Typical fully-saponified polyvinyl alcohols which can be suitably used are described, for example, in Cline et al. U.S. Patent 2,636,803.

The partially-saponified or partially-esterified polyvinyl alcohol which can be used in accordance with this invention is produced by conventional techniques from polyvinyl esters, such as polyvinyl acetate, by known saponification procedures as described, for example, in Scott et al. U.S. Patent 2,266,996 and Bryant et al. U.S. Patent No. 2,668,809. As is known in the art, a "partially-saponified" polyvinyl alcohol is the product of the hydrolysis of a polyvinyl ester, e.g., polyvinyl acetate, in which less than all of the ester groups, e.g., acetate groups, have been converted to hydroxyl groups. As explained in Scott et al. 2,266,996, the saponification or hydrolysis reaction is stopped by neutralizing the catalyst when the desired percentage conversion has occurred. The partially-saponified polyvinyl alcohols which are suitably used in accordance with this invention are sufficiently saponified that at least about 80% of the ester groups have been converted into hydroxyl groups. The degree of polymerization of the polyvinyl alcohol, may vary widely but is suitably at least about 500. In the case of the polyvinyl alcohol admixed with the polyvinyl alcohol-urea reaction product to form a spinning solution, it is preferred that it contain at least 98 mol percent vinyl alcohol units.

Thus, the polyvinyl alcohol suitably used contains 80 to 100% of vinyl alcohol units. The term "polyvinyl alcohol" as used herein also includes vinyl alcohol copolymers such as completely or partially saponified ethylene-vinyl acetate copolymer such as described in U.S. Patent No. 2,386,347 and in British Patent No. 634,140. The polyvinyl alcohol-urea reaction product should be water soluble and preferably contain 0.1 to 6% by weight of nitrogen. When the nitrogen content is less than 0.1%, it is impossible to obtain the desired improvement in the dyeability whereas when the nitrogen content is above 6%, no further improvement in dyeability is observed.

The nitrogen content in the total polymer component of the spinning solution when the polyvinyl alcohol-urea composition is mixed with polyvinyl alcohol is preferably 0.075 to 4.5% and the above-mentioned improvement in dyeability is not obtained if the nitrogen content is less than 0.075%. On the other hand, when the content is above 4.5%, no further improvement is obtained.

The spinning compositions are spun to form fibers in conventional manner, e.g., by extruding the solutions 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, e.g., 20% to saturation, 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.

Conventional treatments may be applied to the fibers. Thus, 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 cold or after heating to a draw ratio of about 1.1:1 to 9:1 during or after spinning, e.g., in a bath containing the

above-mentioned salts, or in air at room temperature or heated up to 250° C. 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.

Subsequent heat treatment is usually carried out by heating the fibers at constant length in the above-mentioned salt bath at a temperature of 70° C. to the boiling point, or a medium such as air at 150°–250° C., for 2 seconds to 5 minutes, and the fibers may be subjected to heat-shrinking by an amount less than 20%.

The fibers can also be subjected to acetalization in conventional manner, e.g., in an aqueous solution containing 0.05 to 10% of an aldehyde having 1 to 12 carbon atoms, such as formaldehyde, acetaldehyde, chloroacetaldehyde, butyraldehyde, nonylaldehyde, benzaldehyde, monochlorobenzaldehyde, 1-naphthaldehyde, glyoxal, malonaldehyde, glutaraldehyde, terephthalaldehyde, and like aliphatic and aromatic aldehydes, and 0.05 to 30% of a mineral acid such as sulphuric acid, hydrochloric acid or phosphoric acid, or they can be acetalized in an aqueous solution containing the above-mentioned salts, and an organic solvent such as an alcohol, e.g., ethyl alcohol, or a surfactant, at room temperature, or at a temperature up to 100° C., for 1 minute to several hours. The degree of acetalization in the fibers is advantageously 5 to 50 mol percent.

The fibers can also be subjected to other known chemical treatments such as titanation, chroming, periodic acid treatment, and the like. Thus, the fibers may be subjected to treatment in an aqueous solution containing 0.01 to 5% of periodic acid, and 0.5 to 30% of a mineral acid, and it may also contain the above-mentioned salts and an organic solvent, at room temperature, or up to 100° C., for 1 minute to several hours to split the 1,2-glycol linkage in the polyvinyl alcohol.

The polyvinyl alcohol-urea reaction product used can be produced by reacting polyvinyl alcohol with urea in the fused state or in the presence of a solvent such as dimethylformamide. It is more convenient from an industrial viewpoint to effect the reaction in an extrusion zone by extruding a mixture of polyvinyl alcohol and urea while heating the mixture to cause reaction in a conventional extruder at a temperature of 130 to 250° C. and a reaction time of 1 minute to several hours. The extrusion machine, sometimes referred to as an extruding machine, which provides the heated extrusion zone for the carrying out of the heating operation can be any of the various conventional types of extrusion machines commonly used for the extrusion of thermoplastic resins. Typical machines are described, for example in U.S. Patents Nos. Re. 23,839, 2,893,055 and 2,896,253.

The addition of urea to polyvinyl alcohol, suitably in particulate form, e.g., as a powder, can advantageously be effected by mixing the polyvinyl alcohol powder with urea in solution in water or in an organic solvent, or urea in finely-powdered form can be directly mixed with the polyvinyl alcohol powder. After mixing the urea and polyvinyl alcohol to produce a uniform mixture, the mixture is dried to remove the water or the organic solvent.

Various amounts of urea can be mixed with the polyvinyl alcohol to provide the mixture to be subjected to reaction in the extrusion zone. Even when the amount of urea added is less than 10% based on the weight of the polyvinyl alcohol, a nitrogen-containing polyvinyl alcohol derivative of cold-water solubility can easily be produced in a few minutes. Increasing the amount of urea to more than 10% by weight of the amount of polyvinyl alcohol will facilitate reaction in the extrusion zone, and even when the amount of urea is greater than the amount of polyvinyl alcohol, no difficulty will arise in the course of the reaction. In charging the extruding machine with the urea-impregnated polyvinyl alcohol powder, it is desirable that its water content be below 10%. When the water content is more than 10%, there may be some drop in reactivity. However, the desired nitrogen-containing polyvinyl alcohol derivative can be produced when reaction is carried out in a heated extrusion zone without difficulty even when the water content is more than 10%.

The reaction product has a content of combined nitrogen of at least 0.1%, and is soluble in water. Particularly when a very high solubility in cold water is desired, the amount of combined nitrogen is suitably 1%–4%. The minimum amount of urea needed for producing a readily-soluble reaction product is 2% based on the weight of polyvinyl alcohol.

The polyvinyl alcohol-urea reaction product thus obtained is mixed with polyvinyl alcohol in an aqueous solution and the resultant so-called "mixed" spinning solution is spun to produce fibers of greatly increased dyeability and whiteness. The total vinyl alcohol polymer content of the spinning solution is in conformity with the spinning process to be applied, in accordance with conventional techniques. Thus, for wet-spinning, the polymer content is advantageously of the order of 12% to 18%, and for dry-spinning or melt-spinning it is generally of the order of 30% to 35%. When a saccharide is present it is not considered part of the polymer content even if it is a polymer.

As used herein, the term saccharide includes monosaccharides, disaccharides, trisaccharides, tetrasaccharides, commonly characterized as oligosaccharides, as well as polysaccharides. Thus, the water-soluble saccharide to be used in accordance with the invention, includes substances such as glucose, sucrose, starch, dextrin, and the like, and also includes water-soluble vegetable gums such as gum arabic, tragacanth gum, and the like. The water-soluble derivatives of saccharides include methylglucose, acetylglucose, methylsucrose, methylstarch, ethylstarch, carboxymethylstarch, hydroxyethylstarch, cyanoethylstarch, carboxymethylcellulose, carboxyethylcellulose, hydroxyethylcellulose, and the like.

The starch usable in the method of the present invention, is any of the known starches such as potato starch, Japanese arrowroot starch, sweet potato starch, wheat starch, rice starch, corn starch, tapioca starch, arrowroot starch (maranta starch) sago starch and like substances having the starch molecular structure.

It will be understood than any of the known starches and starch derivatives such as those described in "Starch —Its Sources, Production and Uses," by Charles A. Brautlecht (Reinhold Publishing Corp.), can be used.

The amount of the water-soluble saccharide or water-soluble saccharide derivative to be added to the polymers in the spinning solution is preferably less than 35%, based on the polmer content, since no greater improvement in dyeability is observed when more than 35% is used. When water-soluble saccharides or water-soluble saccharide derivatives are added, the amount of nitrogen derived from the urea in the total polyvinyl alchohol content of the solution should preferably be 0.05 to 2.0% since when it is less than 0.05% sufficient improvement in dyeability is not obtained and when it is more than 2.0% no further improvement in dyeability is observed. Within this range the various steps of spinning, drawing, heat-treatment and chemical treatment, as above described, can be carried out substantially as in the case of fibers of polyvinyl alcohol alone. The improvement in dyeability obtainable by combining water-soluble saccharides or water-soluble saccharide derivatives with a mixture of polyvinyl alchohol and polyvinyl alchohol-urea reaction products, as above described, is very high and can not be attained by using these components independently, and the best results can be obtained by the combined use of these two materials with polyvinyl alcohol.

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

To 2 kg. of saponified polyvinyl acetate having a degree of polymerization of 1,700 and containing 98 mol percent of vinyl alchohol units, were added 1 kg. of an aqueous solution containing 200 g. of urea in the course of about two hours and the two solutions were thoroughly mixed. Then the mixture was dried and fed into an extruder a little at a time and extruded while the product was heated and melted at about 200° C. during a residence of about 3 minutes.

Part of the resultant product was dissolved in water, precipitated in methanol, and extracted by means of ethanol to purify it. The content of nitrogen in the thus-treated sample was found to be 1.2%. A mixture of 90 g. of this reaction product, 210 g. polyvinyl alcohol, having a degree of polymerization of 1,700, and 1,700 g. of water were agitated and dissolved at a temperature of from 95 to 100° C. in the course of two hours and the solution was then filtered through a piece of flannel to produce a spinning solution.

The spinning solution was extruded through a nozzle of 0.08 mm. diameter into a saturated sodium sulphate coagulating bath and the fibers produced were 40% stretched and, after drying, they were subjected to heat treatment at 235° C. for 1 minute at constant length, and then formalized in an aqueous solution containing 5% of formaldehyde, 15% of sulphuric acid and 15% of sodium sulphate at 70° C. for 1 hour. The degree of formalization of the formalized fibers was 41 mol percent. The various properties of these fibers are shown in Table I (Sample C). The whiteness, transparency, homogeneity of cross-section and dyeability of the fibers were clearly superior to those of ordinary Vinylon fibers (Sample A) spun from aqueous solution containing polyvinyl alcohol alone and subjected to the same subsequent treatments.

Example 2

The procedure described in Example 1 in the preparation of Sample C was repeated through the heat-treatment step. Then the fibers were benzalized in an aqueous solution containing 1.7% of benzaldehyde, 10% of sulphuric acid and 40% of methanol at 60° C. for 1 hour to provide a degree of benzalization of 24.8 mol percent. The properties of these fibers are shown in Table I (Sample D). These fibers were pure white and highly transparent and had an excellent elastic recovery and a dyeability to direct dyes comparable to that of cotton. These fibers were dyed with 3% (based on the fibers) of the disperse dye, Diacelliton Brilliant Blue BF (C.I. Disperse Blue 3) at 90° C. for two hours and the fibers absorbed 85% of the dyestuff and acquired a deep color comparable to that of cellulose acetate fibers having a tenacity of 1.5 g./denier. On the contrary, when in the present example, β-cyclohexylaminobutyralized polyvinyl alcohol (nitrogen content 1.2%) was used instead of the urea-reaction product, the resulting fibers yellowed badly as shown in Table I (Sample J) and there was less improvement in dyeability.

Example 3

A urea-polyvinyl alcohol product was prepared using the procedure of Example 1, but instead of 200 g. of urea, 500 g. (25% based on the polyvinyl alcohol) of urea were used to produce a product having a nitrogen content of 2.3%. This product was mixed with polyvinyl alcohol and the mixed spinning solution was spun as described in Example I. The fibers produced were subjected to the heat treatment and to benzalization under the conditions described in Example 2, the product having a degree of benzalization of 27 mol percent. The characteristics of these fibers are shown in Table I (Sample E). The fibers were pure white and of high transparency and had excellent dyeability and resilience.

Example 4

Partially saponified polyvinyl acetate having a degree of polymerization of 1,750 and containing 85 mol percent of vinyl alcohol units was reacted with 15% of urea in an extruder for 5 minutes to produce a molten product and then the product was poured into an aqueous solution of methanol and purified. This product had a nitrogen content of 1.5%. It was then mixed with polyvinyl alcohol having a degree of polymerization of 1,700 in a 1:1 ratio and dissolved in water to provide a 15% aqueous solution which was wet-spun. The fibers thus obtained were subjected to heat stretching (100% at 230° C. for 32 seconds) and heat shrinkage (10% at 235° C. for 30 seconds) and were then subjected to formalization or benzalization as in Examples 1 and 2, respectively. Both fiber samples had a high degree of whiteness, excellent transparency, and good dyeability to direct dyes, sulphur dyes, mordant dyes, disperse dyes, basic dyes and azo dyes.

Example 5

A mixture of polyvinyl alcohol having a degree of polymerization of 670, 500% of urea and 500% of dimethylformamide, based on the polyvinyl alcohol, was reacted at 150° C. for 2 hours and then purified. This product had a 3.0% nitrogen content. It was mixed in the amount of 10% with polyvinyl alcohol having a degree of polymerization of 1,600 to produce a wet-spinning solution which was then wet-spun. The resulting fibers were heat-stretched by 230% and heat-treated at constant length at 235° C. They were then treated in an aqueous solution containing 0.5% of sodium periodate, 17% of sulphuric acid and 20% of sodium sulphate at 70° C. for 1 hour. The fibers thus obtained were resistant to hot water (with pressure) of 125° C. and were highly hygroscopic, and had a strain-stress relation similar to cotton. They also exhibited a dyeability to cotton dyes, such as direct dyes, which was superior to that of cotton itself.

Example 6

Urea was reacted with an ethylene-vinyl alcohol copolymer containing 5 mol percent of ethylene units in the manner described in Example 1. Nine hundred grams of the reaction product thus obtained, containing 1.2% of nitrogen, and 2,100 g. of polyvinyl alcohol having a degree of polymerization of 1,700 were dissolved in 6,000 g. of water to produce a spinning solution having a 33% polymer concentration. This spinning solution was dry-spun by extruding it from a spinneret having 30 holes, each of 0.2 mm. diameter, into air. The fibers thus obtained were subjected to formalization or benzalization under the conditions described in Examples 1 and 2, respectively. The two samples of fibers thus obtained did not yellow in contrast to the yellowing of fibers obtained from an aqueous solution containing polyvinyl alcohol only and subjected to similar heat-treatment and acetalization, and the two fiber samples exhibited excellent dyeability to direct dyes and other kinds of dyes.

Example 7

To 2 kg. of a dry powder consisting of saponified polyvinyl acetate having a degree of polymerization of 1,700 and containing 98 mol percent of vinyl alcohol units was added 1 kg. of an aqueous solution containing 200 g. of urea and the solution and the powder thoroughly mixed, then dried and fed a little at a time into an extruder which subjected the mixture to reaction at 200° C. for 3 minutes and extruded the reaction product. 45 g. of the polyvinyl alcohol derivative thus obtained were mixed with 225 g. of the polyvinyl alcohol, having degree of polymerization of 1,700, 22.5 g. of starch and 1680 g. of water, and the mixture was heated and stirred to effect

solution, and was then filtered to produce a spinning solution. This spinning solution was extruded through a nozzle of 0.08 mm. diameter into a saturated sodium sulphate coagulation bath at 45° C., and the fibers thus spun were stretched 400% between rollers and, after drying, were subjected to heat treatment at constant length at 235° C. for 1 hour. They were then subjected to formalization in an aqueous solution containing 5% of formaldehyde, 15% of sulphuric acid and 15% of sodium sulphate at 70° C. for 1 hour, to provide a degree of formalization of 41 mol percent. The fibers thus obtained exhibited a 5% shrinkage in boiling water, a tenacity of 4.0 g./denier and a dye-absorption of 19 mg./g. The depth of color (K/S value at 10 mg./g. dye-absorption) was 11. In contrast to ordinary Vinylon fibers (Sample A) spun from an aqueous solution containing polyvinyl alcohol alone and subjected to subsequent treatments under the same conditions, the fibers of this example had a homogeneous cross-section, a transparent appearance, and excellent dyeability. Their dyeability was superior to that of fibers obtained from a solution of polyvinyl alcohol and starch or a polyvinyl alcohol-urea reaction product.

Example 8

The procedure of Example 7 was repeated through the heat-treatment step. Then the fibers were benzalized in an aqueous solution containing 1.75% of benzaldehyde, 10% of sulphuric acid and 40% of methanol at 60° C. for 1 hour, to produce a degree of benzalization of 23.5 mol percent. The thus-treated fibers exhibited 6% shrinkage in boiling water, a tenacity of 3.6 g./denier, a dye-absorption of 14 mg./g., a depth of color (K/S value at 10 mg./g. dye-absorption) of 10, and their dyeability to direct dyes was excellent and similar to formalized Vinylon. In comparison, fibers (Sample B) obtained from an aqueous solution containing polyvinyl alcohol alone could not be dyed to any substantial extent and when compared with fibers spun from an aqueous solution of starch and polyvinyl alcohol, the fibers of this example had excellent dyeability, particularly depth of color, and they were superior in dyeability to fibers spun from an aqueous solution of the mixture of a polyvinyl alcohol urea reaction product and polyvinyl alcohol. Moreover, when the fibers were dyed with the disperse dye, Diacelliton Brilliant Blue BF, in the amount of 3% (based on the fibers), at 90° C., for 2 hours, the fibers absorbed 90% of the dyestuff and they exhibited a deeper color than the fibers of any of the preceding examples.

Example 9

An aqueous solution of a mixture of 10 parts of a polyvinyl alcohol-urea reaction product similar to that of Example 7, 90 parts of polyvinyl alcohol of a degree of polymerization of 1,500, and 10% (based on the polyvinyl alcohol) of sodium carboxymethyl cellulose (CMC), was spn and the fibers thus obtained wer subjected to 100% roller stretching and, after drying, 400% stretching at 230° C., and 10% hot shrinkage at 235° C. The fibers were then formalized with 5% of formaldehyde and 15% of sulphuric acid at 70° C. for 1 hour. The fibers thus obtained had a tenacity of 8.5 g./denier and their dyeability with a direct dye (Congo red) was clearly superior to that of fibers formed from polyvinyl alcohol alone, and fibers obtained by mixed spinning of a mixture of saccharides and polyvinyl alcohol, or fibers produced from a solution of a polyvinyl alcohol-urea reaction product and polyvinyl alcohol, under the same conditions.

Example 10

Polyvinyl alcohol having a degree of polymerization of 600 was mixed with 30% of urea and the mixture was subjected to reaction and the reaction product was purified. Ten parts of the reaction product, which contained 3.0% of nitrogen, 90 parts of polyvinyl alcohol, having a degree of polymerization of 1,800, and gum arabic in the amount of 10% (based on the total polymer component) were mixed and added to water to form a spinning solution which was spun to form fibers. These fibers were subjected to heat-treatment and then subjected to formalization or benzalization. The two samples of fibers thus obtained had much better dyeability than fibers made of polyvinyl alcohol alone and prepared under the same conditions.

Example 11

Ten parts of a reaction product containing 2.2% of nitrogen obtained by reacting urea with partially-saponified polyvinyl acetate containing 88 mol percent of vinyl alcohol units, were mixed with 90 parts of polyvinyl alcohol having a degree of polymerization of 1,600, and 10% (based on the total polymer component) of glucose and formed into an aqueous spinning solution. This solution was spun and the fibers thus obtained were heat stretched by 250% at 230° C., heat-treated at constant length at 235° C. and treated in an aqueous solution containing 0.5% of sodium periodate, 17% of sulphuric acid and 20% sodium sulphate at 70° C. for 1 hour. The fibers were then immersed in a solution containing 3.5% of benzaldehyde, 10% of sulphuric acid and 40% of methanol at 60° C. for 1 hour, to produce fibers having a degree of benzalization of 32%. These fibers had better water resistance, elongation and resilience when compared with polyvinyl alcohol fibers produced in the same manner, and they exhibited excellent dyeability with Diacellition Brilliant Blue BF (3% based on the fibers) at 90° C. for 2 hours, and they were clear in color.

Example 12

Twenty parts of a reaction product containing 1.1% of nitrogen obtained by reacting urea with saponified polyvinyl acetate containing 98 mol percent of vinyl alcohol units, were mixed with 80 parts of polyvinyl alcohol, having a degree of polymerization of 1,500, 10% of starch (based on the total polymer component) and 10% of sodium sulphate (based on the total polymer component), and the mixture made into a spinning solution which was spun under the conditions described in Example 7. The resulting fibers were subjected to heat treatment and then formalization or benzalization. The fiber samples thus obtained had a homogeneous cross-section of substantially circular shape and had desirable contact feel. Their dyeability to direct dyes was clearly superior to that of fibers made of polyvinyl alcohol alone and produced in similar manner.

Example 13

A mixed aqueous spinning solution containing 5 parts of a reaction product containing 2.2% of nitrogen and obtained by the reaction of urea with polyvinyl alcohol of a degree of polymerization of 1,700, 95 parts of polyvinyl alcohol of a degree of polymerization of 1,600, and 7% (based on total polymer component) of CMC, was spun into a solution of 350 g./l. of sodium sulphate at 55° C. The fibers were air dried and subjected to 700% heat stretching in air at 230° C., then 15% shrinkage in air at 235° C. Then the fibers were acetalized in an aqueous solution containing 0.5% of formaldehyde, 2% of β-cyclohexylaminobutyraldehyde, 15% of sulphuric acid and 10% of sodium sulphate at 60° C. for 2 hours. The thus-treated fibers had a substantially circular cross-section and showed a deep color depth when dyed with acid Brilliant Scarlet 3R (C.I. Acid Red 18), 2% in 1% sulphuric acid at 80° C. for 1 hour. This dyeability was far superior to that of fibers made of polyvinyl alcohol alone and produced in the same manner.

It will be understood that, unless otherwise indicated, conventional operations and conventional apparatus are employed in carrying out the invention including conventional mixing apparatus. Similarly, conventional spinning, dyeing, and fiber-treating techniques and apparatus are suitably employed with respect to fibers produced

from the spinning solutions of this invention. The conditions and the relative relationships set forth in the examples are those preferred in carrying out the invention but it will be understood that other conditions and relationships may be used within the scope of the invention. For example, when a water-soluble saccharide is employed as a component of the spinning solution it is desirable that it be present in an amount of at least 1% based on the other polymer components of the solution. Furthermore, all percentages used in the foregoing description are percentages by weight, unless otherwise indicated.

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. In the manufacture of polyvinyl alcohol fibers, the steps which comprise preparing an aqueous spinning solution comprising a mixture of polyvinyl alcohol and a water-soluble polyvinyl alcohol derivative produced by the reaction of polyvinyl alcohol and urea, said derivative containing 0.1 to 6% of nitrogen derived from said urea, and the nitrogen content of the total polymer component of said solution being 0.05 to 4.5%, and spinning said solution to form fibers therefrom.

2. In the manufacture of polyvinyl alcohol fibers, the steps which comprise preparing an aqueous spinning solution comprising a mixture of polyvinyl alcohol, a water-soluble saccharide, and a water-soluble polyvinyl alcohol derivative produced by the reaction of polyvinyl alcohol and urea, said derivative containing 0.1 to 6% of nitrogen derived from said urea, the nitrogen content of the total polymer component of said solution being 0.05 to 2.0%, and the amount of said water-soluble saccharide being 1 to 35% based on the total vinyl alcohol polymer component, and spinning said solution to form fibers therefrom.

3. A process as defined in claim 1, wherein the polyvinyl alcohol used in forming the polyvinyl alcohol derivative contains at least 80 mol percent of vinyl alcohol units.

4. In the manufacture of polyvinyl alcohol fibers, the steps which comprise preparing an aqueous spinning solution comprising a mixture of polyvinyl alcohol and a water-soluble polyvinyl alcohol derivative produced by the reaction of polyvinyl alcohol and urea, said derivative containing 0.1 to 6% of nitrogen derived from said urea, and the nitrogen content of the total polymer component of said solution being 0.05 to 4.5%, spinning said solution to form fibers therefrom, drawing the fibers at a draw ratio of 1:1.1 to 1:9, subjecting the drawn fibers to hot shrinkage of 0 to 30% at 150 to 250° C. for 1 second to 30 minutes, and acetalizing the fibers with an aldehyde having 1 to 12 carbon atoms.

5. In the manufacture of polyvinyl alcohol fibers, the steps which comprise preparing an aqueous spinning solution comprising a mixture of polyvinyl alcohol, a water-soluble saccharide, and a water-soluble polyvinyl alcohol derivative produced by the reaction of polyvinyl alcohol and urea, said derivative containing 0.1 to 6% of nitrogen derived from said urea, and the nitrogen content of the total vinyl alcohol polymer component of said solution being 0.05 to 2%, and the amount of said water-soluble saccharide being 1 to 35% based on the total vinyl alcohol polymer component, spinning said solution to form fibers therefrom, drawing the fibers at a draw ratio of 1:1.1 to 1:9, subjecting the drawn fibers to hot shrinkage of 0 to 30% at 150 to 250° C. for 1 second to 30 minutes, and acetalizing the fibers with an aldehyde having 1 to 12 carbon atoms.

6. An aqueous spinning solution for use in the manufacture of polyvinyl alcohol fibers of improved characteristics which comprises an aqueous solution containing a mixture of polyvinyl alcohol and a water-soluble polyvinyl alcohol derivative produced by the reaction of polyvinyl alcohol and urea, said derivative containing 0.1 to 6% of nitrogen derived from said urea, and the nitrogen content of the total polymer component of said solution being 0.5 to 4.5%.

7. An aqueous spinning solution for use in the manufacture of polyvinyl alcohol fibers of improved characteristics which comprises an aqueous solution containing a mixture of polyvinyl alcohol, a water-soluble saccharide, and a water-soluble polyvinyl alcohol derivative produced by the reaction of polyvinyl alcohol and urea, said derivative containing 0.1 to 6% of nitrogen derived from said urea, the nitrogen content of the total vinyl alcohol polymer component of said solution being 0.05 to 2.0%, and the amount of said water-soluble saccharide being 1 to 35% based on the total vinyl alcohol polymer component.

8. A spinning solution as defined in claim 6, wherein the polyvinyl alcohol used in forming the polyvinyl alcohol derivative contains at least 80 mol percent of vinyl alcohol units.

9. A spinning solution as defined in claim 7, wherein the polyvinyl alcohol used in forming the polyvinyl alcohol derivative contains at least 80 mol percent of vinyl alcohol units.

10. Polyvinyl alcohol fibers of improved characteristics produced by spinning an aqueous solution containing a mixture of polyvinyl alcohol and a water-soluble polyvinyl alcohol derivative produced by the reaction of polyvinyl alcohol and urea, said derivative containing 0.1 to 6% of nitrogen derived from said urea, and the nitrogen content of the total polymer component of said solution being 0.05 to 4.5%.

11. Polyvinyl alcohol fibers of improved characteristics produced by spinning an aqueous solution containing a mixture of polyvinyl alcohol, a water-soluble saccharide, and a water-soluble polyvinyl alcohol derivative produced by the reaction of polyvinyl alcohol and urea, said derivative containing 0.1 to 6% of nitrogen derived from said urea, the nitrogen content of the total vinyl alcohol polymer component of said solution being 0.05 to 2.0%, and the amount of said water-soluble saccharide being 1 to 35% based on the total vinyl alcohol polymer component.

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NORMAN G. TORCHIN, *Primary Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,200,178 August 10, 1965

Kanji Matsubayashi et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 56, for "deriverative" read -- derivative --; line 62, for "of", third occurrence, read -- or --; column 3, lines 60 to 62, for that portion of the formula reading

R′OCR read R′OCOR

column 5, line 34, for "0.5" read -- 0.05 --; column 9, line 56, for "spn" read -- spun --; same line 56, for "wer" read -- were --; column 12, line 14, for "0.5" read -- 0.05 --.

Signed and sealed this 22nd day of February 1966.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents