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3,044,974

METHOD OF PREPARING POLYVINYL ALCOHOL FILAMENTS CONTAINING STARCH OR DERIVATIVES THEREOF

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This invention relates to an improved process for the production of polyvinyl alcohol filaments. More particularly, the invention relates to an improved wet spinning process for the production of polyvinyl alcohol filaments involving extruding a solution of polyvinyl alcohol in the form of fine streams into a coagulating liquid thereby to form filaments.

Wet spinning techniques for the production of polyvinyl alcohol filaments are known in the art. Generally, filaments produced by such prior wet spinning processes have a kidney-shaped cross section which is composed of distinct skin and core regions. The prior wet spun filaments tend to be somewhat opaque and difficult to dye.

It is an object of this invention to provide an improved wet spinning process for the production of polyvinyl alcohol filaments.

It is a further object to provide for the production by wet spinning of polyvinyl alcohol filaments having improved properties.

Other objects will be apparent from the following description of the invention.

In accordance with this invention, it has now been found that improved polyvinyl alcohol filaments can be wet spun by incorporating starch or a water soluble starch derivative in the polymeric spinning solution and forming filaments from the starch-containing polymer solution by wet spinning techniques. As a result of the incorporation of the starch in the polymer spinning solution, wet spun filaments are obtained which have a more homogeneous cross sectional configuration and which have greatly improved dyeing properties. Filaments produced by the invention tend to be rounder in cross section and more transparent.

The following is illustrative of the advantages obtained through practice of the instant invention:

Polyvinyl alcohol having an average degree of polymerization of 1600 was dissolved in water to form a solution containing 15% by weight polymer. Commercial water soluble potato starch was added in different amounts to various samples of the polymer solution.

The resulting spinning solutions were extruded through a multi hole spinneret into a saturated aqueous coagulating solution of sodium sulfate at 45° C. to form filaments. Coagulating bath immersion length was 1.5 meters, and the filaments exited from the coagulating bath at a speed of 10 meters/minute. The filaments were roller stretched 300%. After air drying at 180° C., the filaments were heated in air at 225° C. for 1 minute. Subsequently, the filaments were formalized in an aqueous bath containing by weight 5% formaldehyde, 15% sulfuric acid, and 15% sodium sulfate for 1 hour.

The elongation, shrinkage in boiling water, and dye absorption when dyed for 1 hour at 80° C. in a bath containing by weight 2% C.I. Direct Violet 51 and 10% sodium sulfate, the weight ratio of dye bath to filament being 50:1, were determined. Also, dyeing concentration value K/S was determined after dyeing to the extent of 10 mg./g. in a bath containing varying concentrations

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of C.I. Direct Brown 1 and 10% sodium sulfate for 2 hours at 80° C., the ratio of bath to filament being 50:1. The dyeing concentration value K/S equals

$$\frac{(1-R_{\infty})^2}{2R_{\infty}}$$

R_{∞} being the reflecting rate at a wave-length of 460 m μ . The following table shows the results obtained:

TABLE I

Sample No.	1	2	3	4	5	6
Amount of Starch in Spinning Solution, percent by weight of Polyvinyl Alcohol.....	0	5	10	20	30	50
Amount of Starch in Filament, percent by weight of Filament.....	0	3.0	5.0	7.0	8.2	11.0
Strength, grams/denier.....	3.5	3.6	3.5	3.4	3.3	2.8
Elongation, percent.....	42	43	43	44	45	62
Shrinkage in Boiling Water, percent.....	5.0	4.2	4.0	2.8	3.8	5.2
Dye Absorption, mg./gram.....	3.7	3.9	4.1	4.2	4.3	5.7
Dyeing Concentration Value.....	1.6	3.8	4.5	5.2	5.5	5.8

These results indicate that the addition of starch to the polymer spinning solution results in the production of filaments having improved dyeing properties. As can be seen from the above, at least about one-third of the added starch is removed from the polyvinyl alcohol during the wet spinning and other process steps. Microscopic examination of the cross sections of the above filaments revealed that sample 1 had the characteristic skin and more configuration of wet spun polyvinyl alcohol filaments; samples 4, 5, and 6 were transparent and had homogeneous cross section. Samples 2 and 3 had substantially less pronounced skin and core cross section than sample 1. The shape of the filament cross section increased in roundness from sample 1 to sample 6; i.e. sample 1 was least round while sample 6 was most round in cross section.

The polyvinyl alcohol employed in the invention preferably consists of at least about 98% vinyl alcohol units. Minor amounts of other monomers can be copolymerized therewith. Blends of polyvinyl alcohol with other material such as amino-acetalized polyvinyl alcohol as described in copending application Serial No. 575,211 of Osugi et al., filed March 30, 1956, now Patent 2,906,594, can be employed.

In carrying out the invention starch is added to the spinning solution in amount sufficient to improve the dyeing properties of filaments prepared therefrom. Generally it is preferred to use at least about 5% starch based on the weight of polyvinyl alcohol polymer. Excessive amounts of starch which cause spinning difficulties or which undesirably affect other filament properties to a significant degree should be avoided. Generally, it is preferred to use about 5–70% based on the weight of polyvinyl alcohol although amounts outside this range can be used. During the wet spinning and/or other wet process steps, at least about one third of the starch is separated from the polyvinyl alcohol. Thus, as indicated in the examples in this specification, the product polyvinyl alcohol filaments contain a considerably lower percentage of starch as compared to the polymer-starch ratio of the spinning solution. Starch or water soluble derivatives of starch including dextrine and the like can be used in the invention.

The spinning solution containing polyvinyl alcohol and starch can be spun to form filaments by known wet spinning methods. An especially preferred spinning technique is described in copending application Serial No. 336,166 of Tomonari et al., filed February 10, 1953, now

Patent 2,988,802. Other wet spinning methods can be used.

After formation of the filaments by wet spinning the filaments can be further treated by stretching, heat treating, acetalization, and the like to produce filaments with desirable and outstanding properties.

The present invention provides a simple, convenient and inexpensive method for producing polyvinyl alcohol fibers having improved dyeing properties by wet spinning techniques. The process of the invention overcomes dyeing difficulties peculiar to previous wet spinning techniques used in the production of polyvinyl alcohol filaments. Spinning techniques other than wet spinning techniques such as described, for example, in U.S. Patent 2,072,302 do not achieve the same advantages as are obtained in practice of the present invention even though starch was suggested for use with polyvinyl alcohol in such other processes since such non-wet spinning processes result in the production of filaments of inferior dyeability whether or not additional material is added to the spinning solution.

The following examples illustrate the invention:

Example 1

An aqueous spinning solution was prepared which contained 20% by weight of a mixture of polyvinyl alcohol having an average degree of polymerization of 1000 and starch. The said starch and polyvinyl alcohol mixture contained 20% starch based on the weight of polyvinyl alcohol. The spinning solution was wet spun to form filaments.

The filaments were water-rinsed and air dried, and then heated in air at 220° C. for 3 minutes. The heat treated filaments were formalized for 2 hours at 60° C. in an aqueous bath containing by weight 3% formaldehyde and 15% sulfuric acid.

The resulting filaments contained 5% by weight starch. The filaments had a homogeneous cross section and were resistant to boiling water. Dye absorption was 5.7 mg./g. under the conditions described above in connection with the results given in Table I.

Example 2

An aqueous spinning solution was prepared containing 12% by weight polyvinyl alcohol having an average degree of polymerization of 2000. The solution also contained dextrine in amount of 40% based on the weight of polyvinyl alcohol. The spinning solution was wet spun to form filaments in a saturated sodium sulfate solution at 45° C. The filaments were roller stretched 400% and dried at 180° C.

The filaments were heated for 2 minutes at 210° C. in superheated steam. Then the filaments were benzalized in an aqueous bath containing 1% dibutyl-naphthalene sodium sulfate, 2% sulfuric acid and benzaldehyde at 60° C. for 30 minutes.

The resulting filaments contained 10% by weight dextrine. The filaments were transparent and of homogeneous cross section. By way of comparison, filaments similarly prepared but without the addition of dextrine had a non-homogeneous cross section. When dyed with Calliton Fast Blue FFR, the filaments prepared with dextrine had much better dyeing characteristics.

Example 3

An aqueous spinning solution was prepared containing 10% by weight of polyvinyl alcohol having an average degree of polymerization of 1600. The spinning solution also contained 70% dextrine based on the weight of polyvinyl alcohol. The spinning solution was spun to form filaments in a saturated sodium sulfate aqueous solution at 50° C. The filaments were air dried, stretched 700% in air at 235° C. and heat shrunk 15%. The filaments were acetalized for 2 hours at 60° C. in a bath containing by weight 0.5% formaldehyde, 2% β -cyclo-

hexylaminobutyraldehyde, 15% sulfuric acid and 10% sodium sulfate.

The acetalized filaments contained 13% by weight dextrine. The filaments of this example and filaments similarly prepared without the addition of dextrine each were dyed in a bath containing by weight 2% acid Scarlet 3R (an acid dyestuff) and 1% sulfuric acid, the weight ratio of bath to filament being 50:1, at 80° C. for 1 hour. Both filaments completely absorbed the dyestuff. The dyed color of the filaments of the invention was greatly superior to that of the other filaments.

Example 4

An aqueous spinning solution was prepared containing 15% by weight of a mixture of polyvinyl alcohol and amino-acetalized polyvinyl alcohol, said mixture having an average degree of amino-acetalization of 1%. The polyvinyl alcohol had an average degree of polymerization of 1600. The amino-acetalized polyvinyl alcohol had been acetalized to a 30% degree of acetalization by reaction with β -cyclohexylaminobutyraldehyde. Starch was added to the spinning solution in amount of 10% based on the weight of the polymer mixture.

The spinning solution was wet spun to form filaments in a saturated aqueous solution of sodium sulfate at 45° C. The filaments were roller stretched 200% and dried. The filaments were benzalized for 1 hour at 60° C. in an aqueous bath containing 2% benzaldehyde, 40% methyl alcohol, and 10% sulfuric acid.

The resulting filaments contained 5.1% by weight starch. The filaments of the example and filaments similarly prepared but without the addition of starch each were dyed in a bath containing by weight 2% acid Scarlet 3R and 10% acetic acid, the weight ratio of bath to filament being 50:1, at 80° C. for 1 hour. Both filaments completely absorbed the dyestuff. The dyed color of the filaments of the invention was greatly superior to that of the other filaments.

Example 5

An aqueous spinning solution was prepared containing by weight 15% polyvinyl alcohol having an average degree of polymerization of 1000. The solution also contained 10% methylized or acetified starch based on the weight of polyvinyl alcohol. The spinning solution was spun to form filaments in a saturated aqueous solution of sodium sulfate at 45° C.

The filaments were heated in air at 220° C. for 1 minute and then formalized in an aqueous bath containing by weight 3% formaldehyde, 10% sulfuric acid, and 15% sodium sulfate for 1 hour at 50° C.

The resulting filaments contained about 5% by weight starch. The filaments were transparent and had superior dyeing characteristics when compared to filaments similarly prepared but without starch addition.

Example 6

An aqueous spinning solution was prepared which contained by weight about 14% polyvinyl alcohol having an average degree of polymerization of 1500. The solution also contained 20% starch based on the weight of polyvinyl alcohol. The spinning solution was spun to form filaments in an aqueous coagulating bath containing 300 grams/liter sodium sulfate and 100 grams/liter aluminum sulfate. The resulting filaments were immersed in a sodium sulfate solution at 100° C. for 2 hours.

The filaments contained 6% by weight starch. The filaments were transparent and had superior dyeing properties when compared to filaments similarly prepared but without starch addition.

Example 7

An aqueous spinning solution containing by weight 15% polyvinyl alcohol having 1700 average degree of polymerization and 5% starch based on the weight of polyvinyl alcohol was spun into filaments in an aqueous satu-

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rated sodium sulfate solution at 50° C. The filaments were heated at 230° C. and subsequently treated 15 minutes without stretching in hot water at 85° C. The filaments were formalized in an aqueous bath containing by weight 5% formaldehyde, and 15% sulfuric acid at 60° C. for 1 hour.

The filaments contained 3% by weight starch and had superior dyeing properties when compared to filaments similarly prepared but without starch addition.

Example 8

An aqueous spinning solution containing by weight 13% polyvinyl alcohol having 1600 average degree of polymerization and also containing 1% brew paste and 15% starch based on the weight of polyvinyl alcohol was prepared. The spinning solution was spun into filaments in a saturated aqueous sodium sulfate solution at 45° C.

The filaments were cut into 3 inch lengths, and heated to 225° C. for 5 minutes. The cut filaments were then formalized in an aqueous bath containing by weight 5% formaldehyde, 20% sulfuric acid and 20% sodium sulfate at 70° C. for 1 hour.

The product cut filaments contained about 6% by weight starch and were about 3 times better in dyeability than filaments similarly formed but without starch addition.

Example 9

An aqueous spinning solution containing by weight 15% polyvinyl alcohol having 1700 average degree of polymerization and also containing 20% starch based on the weight of polyvinyl alcohol was prepared. The spinning solution was spun into filaments in a saturated aqueous sodium sulfate coagulating solution at 75° C. The filaments were heated in air at 235° C. and then formalized in an aqueous bath containing by weight 5% formaldehyde, and 20% sulfuric acid at 65° C. for 1 hour.

The product filaments contained about 7% by weight starch. The filaments were rounder in cross section and of superior transparency and dyeability when compared to filaments similarly prepared but without starch addition.

Example 10

An aqueous spinning solution containing 14% by weight polyvinyl alcohol of 1700 average degree of polymerization and also containing 20% of amidoxime starch based on the weight of polyvinyl alcohol was spun into filaments in an aqueous coagulating solution containing 400 grams/liter of sodium sulfate. The filaments were heated in air at constant length at 220° C. for 30 seconds. The filaments were then formalized in an aqueous bath containing by weight 5% formaldehyde, 15% sulfuric acid and 15% sodium sulfate at 65° C. for 1 hour.

The filaments contained 6% by weight of amidoxime

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starch and were superior in dyeing properties to filaments similarly prepared but without starch addition.

We claim:

1. The method of preparing polyvinyl alcohol filaments having improved dyeing properties which comprises forming an aqueous spinning solution containing polyvinyl alcohol, said polyvinyl alcohol consisting of at least about 98 mol percent vinyl alcohol, and from 5 to 70 percent based on the weight of polyvinyl alcohol of a material selected from the group consisting of starch and water-soluble materials derived from starch, and wet spinning said solution into a coagulating liquid to form filaments.

2. The method of claim 1 wherein said material is starch.

3. The method of claim 1 wherein said coagulating liquid is an aqueous sodium sulfate solution.

4. The method of preparing polyvinyl alcohol filaments having improved dyeing properties which comprises forming an aqueous spinning solution containing polyvinyl alcohol, said polyvinyl alcohol consisting of at least about 98 mol percent vinyl alcohol, and from about 5 to 70 percent based on the weight of polyvinyl alcohol of a material selected from the group consisting of starch and water-soluble materials derived from starch, extruding the spinning solution in the form of fine streams into an aqueous coagulating bath, coagulating said fine streams, and obtaining polyvinyl alcohol filaments of improved dyeability.

5. The method of preparing polyvinyl alcohol filaments having improved dyeing properties which comprises forming an aqueous spinning solution containing polyvinyl alcohol, said polyvinyl alcohol consisting of at least about 98 mol percent vinyl alcohol, and from about 5 to 70 percent based on the weight of polyvinyl alcohol of a material selected from the group consisting of starch and water-soluble materials derived from starch, extruding the spinning solution in the form of fine streams into an aqueous coagulating bath, coagulating said fine streams, and obtaining polyvinyl alcohol filaments of improved dyeability, the amount of said material selected from the group consisting of starch and water-soluble materials derived from starch in said filaments being at least one third less than the amount contained in said spinning solution based on the weight of polyvinyl alcohol.

References Cited in the file of this patent

UNITED STATES PATENTS

2,127,896	Vohrer	Aug. 23, 1938
2,146,295	Herrmann et al.	Feb. 7, 1939
2,250,681	Schwartz	July 29, 1941
2,265,283	Herrmann et al.	Dec. 9, 1941
2,716,049	Latour	Aug. 23, 1955