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WET SPINNING POLYVINYL ALCOHOL PROCESS

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This invention relates to a method of manufacturing synthetic fibers of polyvinyl alcohol having homogeneous cross section by an improved wet spinning process. More particularly, this invention relates to an improved method of wet spinning polyvinyl alcohol to form fibers using a coagulating bath containing water soluble sulfate as the major coagulating ingredient and also containing water soluble thiocyanate as an additional bath ingredient.

In the manufacture of polyvinyl alcohol by previously known wet spinning techniques wherein water soluble sulfates such as sodium sulfate or ammonium sulfate are the essential coagulating salts, fibers are obtained which do not have a homogeneous cross section but which have a distinct skin and core cross sectional configuration. The skin and core configuration of such fibers cause the fibers to be opaque. Additionally, the skin and core configuration gives rise to difficulties in dyeing. The color tone is somewhat inferior and tends to be somewhat unstable with fibers having this distinct skin and core configuration.

Polyvinyl alcohol fibers having homogeneous cross section can be obtained by spinning polyvinyl alcohol into a gaseous medium such as air thereby to remove water. Such fibers have somewhat better dyeability and color stability as contrasted with fibers prepared by conventional wet spinning processes. However, disadvantages accompanying such spinning techniques make it desirable to have a wet spinning process whereby polyvinyl alcohol fibers having homogeneous cross section can be readily obtained.

It is an object of the present invention to provide an improved wet spinning process for the production of polyvinyl alcohol fibers having homogeneous cross section.

Other objects will be apparent from the following description of the invention. In accordance with the present invention, polyvinyl alcohol fibers having homogeneous cross section are prepared by a wet spinning process involving extruding an aqueous solution of the polyvinyl alcohol into a coagulating bath which contains water soluble thiocyanate salt in addition to the normal coagulating salt such as sodium sulfate. Fibers obtained by the present invention have superior dyeing characteristics.

The following example illustrates the effect of practice of the present invention.

A 15% aqueous solution of polyvinyl alcohol having polymerization degree of 1600 was used as spinning solution, and four kinds of coagulating baths, (*a*) 380 g./l. of Glauber's salt, (*b*) 380 g./l. of Glauber's salt+5 g./l. of potassium thiocyanate, (*c*) 380 g./l. of Glauber's salt+10 g./l. of potassium thiocyanate, and (*d*) 380 g./l. of Glauber's salt+20 g./l. of potassium thiocyanate are used respectively at 45° C. and spun through the coagulating bath with a length of 1.5 m. at a speed of 10 m./minute and subjected to the roller-stretch of 200% and obtained the single filament of 5 denier and a tow of 1000 filaments. After the filaments thus obtained were air-dried, they were heat treated in air at 215° C. for one minute and formalized in the aqueous solution containing 5% of formaldehyde, 15% of sulfuric acid and 15% Glauber's salt for one hour at 60° C. The filaments thus obtained were dyed in an ordinary dyeing

bath containing 2% Direct Green BD for one hour at 70° C., and the dyeability was measured and obtained the value of "F" from the reflection rate by the formula of Kubelka-Munk

$$F=\frac{(1-R)^2}{2R}$$

where R is the reflection rate. The result thereof is shown in the following table. Further for the sake of reference the results of the filaments spun by a dry spinning process and subjected to heat treatment and formalization by the similar conditions as above described are shown together with those of viscose rayon staple fibers on the market.

	(*a*)	(*b*)	(*c*)	(*a*)	Spun by dry process	Viscose S.F.
Formalization degree	33	32	33	35	30	--------
Shrinkage in water at 100° C. for 30 min. (percent)	0.8	0.5	1.2	1.6	2.5	--------
Strength (g./d.)	3.1	3.2	3.0	2.9	2.9	2.6
Dye absorbing amount (mg./g.)	7.8	8.0	8.2	8.5	7.6	13.6
F	2.4	3.0	3.3	3.7	3.7	4.5
F+	2.7	3.4	3.6	3.8	3.9	4.0

(F+ shows the value of F of dyeing samples when the concentration of dyestuff is changed and the dye absorbing amount is 10 mg./g.).

The results presented above clearly indicate the significant improvement in dye absorption obtainable in practice of the invention. A comparison of the F values illustrates the improvement obtainable through the use of water soluble thiocyanate salts in the wet spinning process. Where dissimilar samples are concerned, it is somewhat difficult to judge the relative dyeability of the samples from the F value. However, naked eye observations of such samples indicate results which are in the same relation of the F values presented in the above table.

The following specific examples illustrate the invention.

Example 1

Spinning solution of polyvinyl alcohol having an average polymerization degree of 1600 and 15% concentration was spun through an immersion length of 1.5 m. in a coagulating bath comprising 380 g./l. of Glauber's salt and 30 g./l. of potassium thiocyanate at 45° C. at the speed of 10 m./minute and wound up after stretching by 200% by rollers.

After being air dried at 220° C. for one minute and heat treated in air they were acetalized at 60° C. for one hour in an aqueous solution comprising 5% formaldehyde, 15% sulfuric acid and 15% Glauber's salt and washed with water and dried.

Observing the cross section of the fiber thus obtained by an optical microscope no skin-core configuration was recognized at all and the fiber was transparent in appearance and dyed well wih an absorbing dyestuff. The fiber showed clean color, and did not discolor by after treatment such as ironing.

Example 2

To an aqueous solution of polyvinyl alcohol having an average degree of polymerization of 1600 which solution contained 15% by weight of polyvinyl alcohol was added 15% of sodium sulfate based on the weight of polyvinyl alcohol contained therein. This solution was extruded into a coagulating bath containing 380 g./l. sodium sulfate and 20 g./l. ammonium thiocyanate to form fibers. The fibers were heat treated and acetalized as described in Example 1. Fibers having substantially homogeneous and circular cross sections were obtained.

Example 3

An aqueous solution containing 15% by weight of polyvinyl alcohol having an average degree of polymerization of 1600 was prepared. Polyvinyl alcohol which had been amino-acetalized to a 20% degree of acetalization by reaction with β-cyclohexylaminobutyraldehyde was added to the solution in amount of 6.5% based on the weight of polyvinyl alcohol contained therein. The resulting spinning solution was extruded into a coagulating bath containing 380 g./l. of sodium sulfate and 5 g./l. of potassium thiocyanate to form fibers. The resulting fibers were heat stretched in air at 220° C. 60% for one minute and subsequently subjected to 10% shrinkage in air at 230° C. for one minute. The resulting fibers were acetalized as described in Example 1. Fibers having good dyeability and the characteristic of dyeing to a clear color were obtained.

Example 4

Polyvinyl alcohol having an average degree of polymerization of 1200 was dissolved in water to form a 16% solution. To the solution was added polyvinyl alcohol which had been acetalized with β-aminopropionaldehyde to an acetalization degree of 20% in amount of 11.8% based on the polyvinyl alcohol. 15% of sodium sulfate based on the weight of polyvinyl alcohol was also added to the solution. This mixed spinning solution was extruded in a coagulating bath containing 380 g./l. sodium sulfate and 10 g./l. potassium thiocyanate to form fibers. The resulting fibers were dried and heat stretched at 205° C. in two seconds 80% of their length in a Wood's alloy bath. The stretched fibers were subjected to heat shrinkage of 20% in 5 seconds at 210° C. in a Wood's alloy bath. The resulting fibers were acetalized as described in Example 1. Fibers having good dyeability and circular and homogeneous cross sections were obtained.

Example 5

An aqueous spinning solution containing 18% by weight of polyvinyl alcohol having an average degree of polymerization of 1600 was extruded into a coagulating bath containing 500 g./l. ammonium sulfate and 20 g./l. ammonium thiocyanate to form fibers. The fibers were dried and heat stretched 20% of their length. The stretched fibers were heat treated at constant length and subsequently acetalized in an aqueous bath containing by weight 1% benzaldehyde, 5% sulfuric acid, and 0.5% lauryltrimethyl-ammonium chloride at 65° C. for one hour. The fibers obtained had superior elastic properties and had homogeneous cross section. The fibers could be dyed to a clear color, and there was substantially no discoloration after subsequent treatment after ironing.

Example 6

An aqueous spinning solution containing 25% by weight of polyvinyl alcohol having an average degree of polymerization of 1000 was extruded into an aqueous coagulating bath containing 300 g./l. sodium sulfate, 50 g./l. sodium chloride, and 15 g./l. sodium thiocyanate to form fibers. The fibers were roller-stretched 300% and subsequently heat treated and acetalized by reaction with formaldehyde. Fibers having homogeneous cross section were obtained.

Example 7

An aqueous spinning solution containing by weight 15% of polyvinyl alcohol having an average degree of polymerization of 1600 was extruded into an aqueous coagulating bath containing 380 g./l. sodium sulfate and 30 g./l. potassium thiocyanate to form fibers. The fibers were stretched in a second bath containing 300 g./l. sodium sulfate at 90° C. and then wound up. The fibers thus obtained were heat treated under tension in a saturated aqueous solution of sodium sulfate at 125° C. for one hour and subsequently acetalized. Fibers having a uniform, homogeneous cross section were obtained.

In practice of the present invention known wet spinning techniques can be employed. Especially preferred wet spinning conditions are described in copending application Serial No. 336,166, filed February 10, 1953, of T. Tomonari et al. Other wet spinning techniques can be employed.

In accordance with the invention water soluble thiocyanates are incorporated in the coagulating bath. Specific examples of suitable water soluble thiocyanates are sodium thiocyanate, potassium thiocyanate, ammonium thiocyanate and the like. The thiocyanate can be used in varying amounts in carrying out the invention. However, it is usually preferred to use at least 5 g./l. and preferably 10 g./l. or more of the thiocyanate.

Water soluble sulfate salts are the preferred coagulating salts used in carrying out the invention. However, known coagulating salts can also suitably be employed. Examples of such salts are given in copending application Serial No. 336,166 previously referred to hereinabove.

We claim:

1. The method of preparing polyvinyl alcohol fibers having a homogeneous cross section which comprises forming an aqueous spinning solution of polyvinyl alcohol and extruding the said spinning solution into an aqueous coagulating bath simultaneously containing a water soluble thiocyanate salt to form fibers in the presence of said thiocyanate.

2. The method of preparing polyvinyl alcohol fibers having a homogeneous cross section which comprises forming an aqueous spinning solution of polyvinyl alcohol and extruding the spinning solution into an aqueous coagulating bath containing a water soluble sulfate coagulating salt and simultaneously containing a water soluble thiocyanate to form fibers in the presence of said thiocyanate.

3. The method of claim 2 wherein the water soluble thiocyanate is sodium thiocyanate.

4. The method of claim 2 wherein the water soluble thiocyanate is potassium thiocyanate.

5. The method of claim 2 wherein the water soluble thiocyanate is ammonium thiocyanate.

6. An aqueous coagulating bath adapted to form polyvinyl alcohol fibers having a homogeneous cross section from an aqueous spinning solution of polyvinyl alcohol which comprises an aqueous solution containing a water-soluble coagulating salt and simultaneously containing a water-soluble thiocyanate salt.

7. An aqueous coagulating bath adapted to form polyvinyl alcohol fibers having a homogeneous cross section from an aqueous spinning solution of polyvinyl alcohol which comprises an aqueous solution containing a water-soluble sulfate coagulating salt and simultaneously containing a water-soluble thiocyanate salt.

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