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# METHOD OF MANUFACTURING SYNTHETIC FIBER OF POLYVINYL ALCOHOL HAVING EXCELLENT PROPERTIES

Kenichi Tanabe and Tadao Ashikaga, Kurashiki, Japan, assignors to Kurashiki Rayon Company Limited, Kurashiki, Japan, a corporation of Japan

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## ABSTRACT OF THE DISCLOSURE

The invention relates to a method for manufacturing uniform polyvinyl alcohol fibers which involves spinning an aqueous solution of polyvinyl alcohol into a 10–30% caustic coagulating bath. The polyvinyl alcohol employed should have the characteristics of low water swelling.

The present invention relates to a method of manufacturing synthetic fibers of polyvinyl alcohol characterized in that an aqueous solution consisting essentially of polyvinyl alcohol (hereafter identified as PVA) less than 2.0 of swelling degree of the film prepared at 30° C. in water at 30° C. (hereafter identified as water swelling degree, which is expressed by

$$\frac{\text{The weight of film after swelled} - \text{The weight of dried film after swelling}}{\text{The weight of dried film after swelling}}$$

is used as the spinning solution and an aqueous solution of caustic alkali is used as the coagulating agent. The polyvinyl alcohol is spun at a temperature less than 50° C. and subjected to neutralization, water-washing and drying successively, then stretched and, if necessary, subjected to heat treatment or chemical treatment.

The principal object of the invention is to manufacture in simple and easy manner synthetic PVA fibers which have circular and uniform cross section and excellent dyeability without substantial change in mechanical properties, dimensions and texture when wetted.

The synthetic fibers of PVA manufactured by wet spinning process using salt bath, such as, Glauber's salt or ammonium sulfate etc. have flat cross section, transparent skin layer, and spongy core portion. Due to the non-homogeneous structure the PVA fibers made by a conventional wet spinning process is less dyeable so that it is impossible to obtain clear color tone. Further, due to the existence of granular structure in the inside the Young's modulus is reduced when the fiber is dipped in water. Accordingly, various attempts have heretofore been tried to obtain fibers of uniform and compact structure having no-spongy structure, but in most of them various addition agents were added to the spinning solution or coagulating bath, or they were difficult in the condition of commercial application.

It is well known that the PVA fibers having circular uniform cross section can be obtained by spinning aqueous solution of PVA into a caustic alkali bath, yet, in order to obtain fibers having excellent whiteness by subjecting it to dry heat treatment by a conventional process it is necessary to perfectly neutralize caustic alkali with an acid under a suitable swelled condition, and to remove salts and acids by washing with water, thereby making the fibers slightly acidic, then to dry the fiber. Yet when PVA of more than 2.0 of swelling degree is spun by such a process tacky fibers are produced, thereby spoiling the spinnability considerably. On the other hand, when the



raw PVA having less than 2.0 of water swelling degree and rich in syndiotactic portion is used there is no fear of sticking and provides fiber having excellent opening property and spinnability and also its cross section is naturally circular and uniform, and moreover, improvement of compactness and various properties in wet state, PVA fibers which do not change dimensions, Young's modulus, texture and the like properties in boiling water, and very stable when wetted, can be obtained. Moreover a moderate hygroscopicity of the fiber is not substantially lost, such hygroscopicity being one of the important characteristics of synthetic fibers of PVA not found in other synthetic fibers. The remarkable difference by using such raw PVA material in case of an ordinary wet spinning process could never be substantially recognized but it was attained at first by using caustic alkali as the coagulating bath.

According to the method of the invention, use is made of an aqueous solution having as the essential ingredient PVA containing a large amount of syndiotactic portion as a spinning solution and also the solution mixed with water soluble polymer or emulsifiable polymer in addition may also be used. As the coagulating bath caustic alkalis, such as caustic soda or caustic potash, may be used and its concentration should be limited within the range of 10 to 30% and the temperature of the coagulating bath should be limited to less than 50° C. At less than 10% of caustic alkali the fiber sticks due to the insufficient coagulation, while above 30% the fiber becomes brittle so that both of them are not suitable. Good spinning condition can be assured within the range of 10 to 30% only. Addition of salts of less than 5% to the coagulating bath is possible, yet it is preferable to use a less quantity since at above 5% the effects of the invention is lost. At a coagulating temperature of higher than 50° C. the transparency of the fiber is lost and granular structure develops in its inside so that the coagulating temperature should be lower than 50° C.

The effect of the invention as above described will be explained by means of an example as follows:

An aqueous solution of 18% concentration of PVA (A–PVA) having average degree of polymerization of 1,700 and having water swelling degree of 2.5 obtained by saponifying polyvinyl acetate polymerized by a conventional process and PVA (B–PVA) of average degree of polymerization of 1,700 having water swelling degree of 1.4 obtained by saponifying polyvinyl acetate by photo-polymerization is used as a spinning solution which is extruded through spinnerets of 0.08 mm. dia. and 3,000 holes into an aqueous solution of caustic soda having a concentration of 300 g./l. at 35° C. and taken out of the bath with the dipping length of 1.5 m. and departure speed of 10 m./min., then stretched for 3.0 times between the first roller and second roller. Successively the fiber is neutralized in the second bath circulated with an aqueous solution containing 250 g./l. Glauber's salts and 80 g./l. of sulfuric acid at 30° C. for 30 seconds, and further washed with water in the third bath for 1 minute by flowing water, then dried by infrared rays, then subjected to heat treatment under a constant length in air at 230° C. for 1 minute and crimped by mechanical means and cut off and acetalized in a bath containing 3% of benzaldehyde, 10% of sulfuric acid, 40% of methanol and 47% of water for 60 minutes. In case of B–PVA which has higher water resistance after the heat treatment than that of the A–PVA it is difficult to proceed directly to benzalization. The fiber was pre-treated, before subjecting to benzalization, in 2% aqueous solution of boric acid at 80° C. for 30 minutes. The water resistance of the fiber thus obtained (temperature of water when the fiber contracts 10% loaded with 0.02 g./d.) tenacity, elonga-

tion and Young's modulus in warm water at 80° C. are shown in the following table:

| PVA | Degree of benzalization (mol percent) | Water resistance (° C.) | Dr. | Tensile strength (g./d.) | Elongation (percent) | Knot-strength (g./d.) | Young's Modulus (kg./mm. $^2$) | Reduction rate of Young's modulus in warm water at 80° C., percent | Spinnability |
|---|---|---|---|---|---|---|---|---|---|
| A | 23.8 | 105 | 3.02 | 2.9 | 25.3 | 2.2 | 500 | 80 | Bad, many naps. |
| B | 24.1 | 115 | 2.96 | 3.3 | 24.5 | 2.4 | 550 | 40 | Good. |

As apparent from the results of the above table, the fiber obtained from PVA having low water swelling degree has good water resistance with less reduction of Young's modulus in warm water and the dimensional stability in warm water is exceedingly superior. The PVA obtained by a conventional polymerization has poor spinnability owing to sticking of fibers and there are many naps, whilst the fiber obtained from the PVA of small swelling degree has good opening property so that the spinnability in also good and the spun yarn has also good appearance.

Another speciality of the invention is that the spinnability is superior to that of wet spun filament using an ordinary salt bath and from very thin filament to a thick filament they can easily be spun and after spun from 0.1 dr. to 150 dr. can be easily treated without substantial trouble. This is a great difference compared with the spinning in Glauber's salt bath, wherein spinning is possible from 1 dr. to 75 dr.

If the fiber spun from PVA having swelling degree less than 2.0 in the caustic alkali bath is neutralized, water-washed and dry heat stretched, the fiber having tenacity more than 12 g./d. and resistance to boiling water at more than 120–125° C. can be obtained without subjecting to acetalization and this fiber can be practically used in the state of non-acetalized fiber.

The invention will be further explained in detail by means of examples.

*Example 1*

A 20% aqueous solution of PVA having average degree of polymerization of 1,300 and water swelling degree of 1.6 was spun into an aqueous solution containing 23% of caustic soda at 35° C. and wound up at a departure speed of 15 m./min. and dipping length of 1.5 m. and after the filament was stretched for about 3 times between the first and second rollers, and passed through a tank in which circulates an aqueous solution containing 250 g./d. of Glauber's salt and 100 g./l. of sulfuric acid at room temperature in 30 seconds to neutralize the fiber, and successively washed with water in the next tank for 1 minute, dried by infra-red rays, then subjected to heat treatment under a constant length in air at 230° C. To the fiber is given mechanical crimping, then cut and benzalized by means of a solution consisting of benzaldehyde 5%, sulfuric acid 10%, methanol 40% and water 45% at 60° C. for 1 hour. The fiber thus obtained has circular and uniform cross section and when it is dyed with dispersion dyestuff showed considerably superior dyeing density and had beautiful color tone. Young's modulus under the wet condition was not substantially reduced if compared with that of dry state and also the fiber resists boiling water at 115° C.

*Example 2*

A 18% aqueous solution of PVA having average degree of polymerization of 1,700 and water swelling degree of 1.3 was used as the spinning solution and spun into a coagulating solution containing 25% of caustic soda and taken up at a departure speed of 20 m./min. and dipping length of 1.5 m. at a temperature of 40° C. and after streaching for 2 times between the first and second rollers neutralized in a tank circulated with an aqueous solution containing 200 g./d. of Glauber's salts and 50 g./d. of sulfuric acid at 30° C. for 1 minute. Then the fiber was washed with water in the next tank for 1 minute, then further stretched for 25% and dried and subjected to heat treatment under a constant length in air at 230° C. for 30 seconds. The fiber thus treated was dipped in an aqueous solution containing 2% of boric acid at 70° C. for 30 minutes to swell, then washed with flowing water for 30 minutes to sufficiently remove the boric acid and after squeezing liquid the fiber was benzalized in a bath containing 3% of benzaldehyde, 10% of sulfuric acid, 40% of methanol and 47% of water at 60° C. for one hour. The fiber thus obtained showed soft touch and good dimensional stability.

The dyeability of Celliton Dyestuff was good and showed clear color tone.

*Example 3*

An aqueous solution containing 18% of PVA having average polymerization degree of 2,200 and swelling degree of 1.8 was used as the spinning solution which was spun into a coagulating bath containing 20% of caustic potash of 30° C. with a departure speed of 16 m./min. and dipping length of 1.0 m. Then the fiber after stretched for 2.5 times between the first and second rollers was neutralized, water washed and dried similarly to those of Examples 1 and 2. The fiber was heat stretched for 100% in air at 230° C. for 30 seconds. The fiber resisted boiling water at 110° C. by the heat stretch only. The fiber was treated in an aqueous solution containing 5% phenol at 80° C. for 60 minutes, then washed with warm water at 80° C. and after squeezing the liquid benzalized in a bath containing 3% of benzaldehyde, 10% of $H_2SO_4$, 40% of isopropyl alcohol and 47% of water at 60° C. for one hour.

The fiber thus obtained has high Young's modulus and soft touch and is very stable in hot water.

*Example 4*

A 20% aqueous solution of PVA having average polymerization degree of 1,700 and water swelling degree of 2.0 was used as the spinning solution and spun into a coagulation bath containing 25% of caustic soda at 30° C. with departure speed of 15 m./min. Then the fiber was stretched for 300% and neutralized, washed with water and dried, then further heat stretched for 100% at 235° C. in air for 10 seconds, then further heat treated by giving 15% shrinkage in 10 seconds at 240° C.

The fiber thus obtained was formalized in an aqueous solution containing 5% of formaldehyde and 15% of sulfuric acid at 60° C. for 30 minutes.

The fiber thus obtained had circular uniform cross section and superior dyeability to the fiber obtained in Glauber's salt and had very fine color tone and also high Young's modulus and toughness and excellent dimensional stability.

*Example 5*

A 22% aqueous solution of PVA having average degree of polymerization of 1,200 and water swelling degree of 1.6 was used as the spinning solution and spun into a coagulating bath containing 20% caustic soda at 35° C. with departure speed of 20 m./min. The fiber was stretched for 300%, then neutralized, water washed and dried, then wound up once on a bobbin to provide filament yarn of

120 dr./100 filaments, then the yarn thus obtained was subjected to heat treatment under a constant length in air at 235° C. for 5 seconds and then again wound up on a bobbin. The yarn under the wound state was subjected to formalization treatment and dried without finishing treatment. The filament yarn thus obtained, the monofilament having circular and uniform cross section, has very soft touch and luster resembling natural silk and the dyeability was much better than ordinary wet fiber spun in Glauber's salt bath and moreover, it had high water resistance and Young's modulus and exceeding good dimensional stability.

What we claim is:

1. A method for manufacturing fibers from polyvinyl alcohol which comprises spinning an aqueous solution of polyvinyl alcohol into an aqueous caustic solution at below about 50° C., the caustic solution containing a concentration of 10–30% caustic; thereafter neutralizing the



fibers by passage through an acid containing bath, the polyvinyl alcohol having a water swelling degree of less than about 2.0 as measured by subjecting a film of the polyvinyl alcohol prepared at 30° C. to water at 30° C., the ratio of the water absorbed to the weight of the dried film being the numerical value of water swelling degree.

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ALEXANDER H. BRODMERKEL, *Primary Examiner.*

J. H. WOO, *Assistant Examiner.*