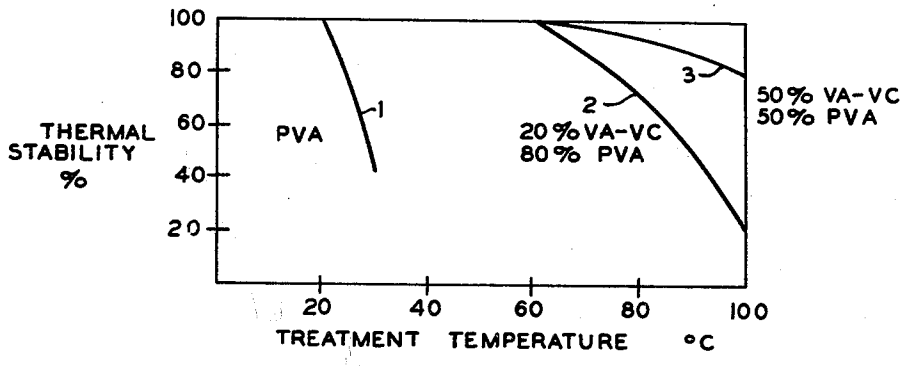
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SPINNING SOLUTIONS OF A MIXTURE OF POLYVINYL ALCOHOL AND A VINYL ACETATE-VINYLIDENE CYANIDE COPOLYMER IN DIMETHYL SULFOXIDE AND FIBERS THEREFROM

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SPINNING SOLUTIONS OF A MIXTURE OF POLYVINYL ALCOHOL AND A VINYL ACETATE-VINYLIDENE CYANIDE COPOLYMER IN DIMETHYL SULFOXIDE AND FIBERS THEREFROM

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This invention relates to the production of synthetic fibers having high mechanical properties, and particularly high elasticity and dyeability, and the invention is more particularly concerned with the production of synthetic fibers from a mixture of polyvinyl alcohol and an interpolymer or copolymer of vinyl acetate and vinylidene cyanide.

Commercial fibers are produced by spinning an aqueous solution of polyvinyl alcohol and then heat-treating and formalizing the resultant fibers by known methods. The commercial fibers are called vinylon and are well-known for their excellent mechanical properties, particularly their strength. For the further improvement of the properties of vinylon, various methods and means have been suggested, including the treatment with higher aldehydes such as benzaldehyde, mixed spinning by means of a resinous emulsion, mixed spinning with basic polymers, mixed spinning with water-soluble polymers, graft-polymerization, and the like.

It is an object of the present invention to provide means for improving the coefficient of elasticity, feel, and dyeability of fibers based on polyvinyl alcohol for the purpose of rendering them more suitable for clothing use.

This and other desirable objects are achieved in accordance with the present invention by preparing a fiber spinning solution composed of a mixture of polyvinyl alcohol and a vinyl acetate-vinylidene cyanide copolymer dissolved in dimethylsulfoxide, and spinning this solution by forcing it into a coagulating bath through a nozzle or spinneret to form filaments, and then, if desired, subjecting the thus-formed fibers to physical or chemical treatments such as stretching, heat-treatment, contraction, acetalization, and the like.

The copolymer of vinyl acetate and vinylidene cyanide (hereinafter referred to as VA–VC copolymer) is an essentially 1:1 alternating copolymer produced by polymerizing vinyl acetate and vinylidene cyanide, as described for example, in Gilbert et al. U.S. Patent 2,615,866. The strength of the fiber obtained by spinning the VA–VC copolymer is relatively weak for a synthetic fiber, but yet its strength is sufficient for practical use. It is also known that its elasticity is considerably higher than that of other vinyl-type synthetic fibers. In addition, its secondary transition point is so high that its thermal properties and hot-water resistance are also very good.

Investigations conducted by us led to the discovery that from a mixed spinning solution of polyvinyl alcohol and VA–VC copolymer in dimethylsulfoxide there could be produced fibers having high mechanical properties and particularly high elasticity and dyeability. It was found that when polyvinyl alcohol and VA–VC copolymer were dissolved in dimethylsulfoxide, almost no eduction-mixing between the polyvinyl alcohol and the copolymer took place, and even when such mixing did occur, the velocity of the eduction-mixing was very slow, making it possible to obtain a sufficiently homogeneous solution suitable for spinning to form fibers. Dimethylsulfoxide has a very powerful dissolving action upon organic substances, and mixes freely with almost all organic solvents and water. Thus, the use of dimethylsulfoxide as the solvent has the further advantage of permitting a free choice of the coagulating bath, so that the coagulating bath can be varied, if desired, within a broad range of composition. The fibers produced from a mixed spinning solution of polyvinyl alcohol and VA–VC copolymer in accordance with this invention may vary in their properties, depending upon the ratio of the polymers, the coagulating bath used, and the like, but the outstanding feature of the fibers is that they have exceptionally good elasticity, thermal stability, and dyeability.

By way of illustration, the relationship between the coefficient of elasticity of fibers, spun and heat-treated under identical conditions and measured under uniform conditions, and the quantity of the VA–VC copolymer is given below. It is to be noted that with low percentages of stretching, the fibers show a higher coefficient of elasticity than pure polyvinyl alcohol fibers. This is because the high elasticity of VA–VC copolymer has manifested itself, and this is clearly shown by the fact that the elasticity increases as the percentage of VA–VC increases.

In the following table, the indicated values were obtained directly after removing the applied weight, the fibers having been heat-treated for 5 seconds at 240° C. after stretching for 400% at 235° C. for 5 seconds.

Content of VA–VC Copolymer (percent) based on total polymer content	Coefficient of elasticity			
	2% stretch	3% stretch	5% stretch	7% stretch
0	64	57	52	51
25	69	62	54	47
50	79	71	57	49

As shown in the accompanying drawing, the thermal stability of the fibers of this invention in hot water is very good. The property of thermal stability referred to was measured in the following manner:

The fiber samples were cut into pieces of 10 cm. in length, and some of them were stretched to 11 cm. After giving them a thermal-stabilizing treatment by immersing them in liquid paraffin at 180°–200° C. for 3 minutes, the stretched and unstretched fibers were measured for change in length upon being subjected to various temperatures of dry heat and of hot water under tension. The differences in length as a result of such exposure were taken as the rate of thermal stability by expressing them in percentages of 1 cm. in relation to the length at the time of thermal stabilization. Fibers with good thermal stability retain their length well, so that their rate of thermal stability is 100%, but in the case of fibers with a poor thermal stability, they readily return to their original length, thus reducing their rate of thermal stability to 0%.

In the case of ordinary vinylon, the rate of thermal stability is good in dry heat, but very poor in hot or even warm water, the rate dwindling almost to 0% in water at 30° C. However, in the case of mixed-spun fibers produced from the spinning solutions of this invention, the rate rises as the mixing ratio is increased, as shown in the drawing, and in hot water of 100° C., the rate of thermal stability has a value of nearly 80%, the fibers thus maintaining almost their original form. It is believed that such improvement in the thermal stability is also due to the manifestation of the characteristics of VA–VC copolymer.

In the accompanying drawing, curve 1 is that of ordinary vinylon which has been thermally-stabilized in liquid paraffin at 180° C. for 3 minutes. Curve 2 is that

of fibers produced from a 20%—80% mixture of VA–VC copolymer and polyvinyl alcohol, the fibers being, after spinning, stretched for 400% at 210° C. for 8 seconds, and after formalization without further heat-treatment, subjected to thermal-stabilization at 200° C. for 3 minutes. Curve 3 is that of fibers from a 50%–50% VA–VC copolymer polyvinyl alcohol mixture in accordance with this invention, the spun fibers being stretched for 400% at 235° C. for 5 seconds, then heat-treated at 240° C. for 5 seconds at a fixed length, and after formalization, subjected to thermal stabilization at 200° C. for 3 minutes.

VA–VC copolymer is known to be hydrophobic, and it was expected that the admixture of this copolymer with polyvinyl alcohol would lower the dyeability of the fibers. However, quite the contrary was found, and spinning from a mixed spinning solution of polyvinyl alcohol and VA–VC copolymer in dimethylsulfoxide produced fibers exhibiting an outstanding improvement in dyeability as compared with fibers of polyvinyl alcohol alone.

The reasons for these surprising and unexpected phenomena with respect to dyeability observed are not fully understood, but it is believed that the yarn is more transparent and homogeneous, free from skin cores, and that the crystallizing tendency of the polyvinyl alcohol has been reduced, since it is a mixed fiber, or that the molecular orientation has been rendered irregular so that it differs from ordinary vinylon, and consequently the dyestuffs can penetrate more easily.

The hot-water resistance of mixed spun fibers produced from mixed polymer spinning solutions of this invention are given in the following table. The fibers were stretched by 400% at 235° C. for 5 seconds and heat treated at 240° C. for 5 seconds. The fibers were then formalized by treatment with formaldehyde in conventional manner.

Percent by weight VA–VC copolymer	Softening Point in water, ° C.	
	After heat-treatment	After formalization
0	100–102	115
25	100	105–107
50	103–105	117.5

As seen in the foregoing table, with a 25% VA–VC copolymer–75% polyvinyl alcohol mixed yarn, the hot-water resistance is lower than that of pure polyvinyl alcohol. With a 50%–50% mixed yarn, it is somewhat higher than pure polyvinyl alcohol. In the case of the 25% VA–VC mixed yarn, apparently the crystallizing property and the orientation of the polyvinyl alcohol have been rendered irregular, resulting in a drop in hot-water resistance. In the case of the 50%–50% mixed yarn, apparently the hot-water resistance is manifested as one of the properties of VA–VC copolymer.

Other samples of mixed spun yarn were stretched 400% at 235° C. for 5 seconds, heat-treated at 240° C. for 5 sec., and formalized, and the Young's modulus was then determined, with the following results:

Percent by weight of VA–VC copolymer	Young's Modulus, g./d.
0	164
25	67
50	43

From the foregoing it will be seen that the Young's modulus of fibers produced in accordance with this invention is lower than that of ordinary vinylon, resulting in advantages such as higher elasticity and a softer feel.

Thus, an important advantage of the present invention

is that fibers are obtained which retain many of the desirable characteristics of VA–VC copolymer yet have additional desirable properties. For example, fibers from a mixture of 1:1 of the two polymers does not show any great difference in mechanical properties as compared with VA–VC copolymer, but its dyeability is outstanding.

The polyvinyl alcohol suitable for use in accordance with the present invention includes polymers composed principally of the vinyl alcohol radical, but is not limited to pure polyvinyl alcohol. Polyvinyl alcohol is a polymer containing hydroxyl groups and corresponding to the formula:

$$(-CH_2-CH)_n \\ | \\ OH$$

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:

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

Typical polyvinyl alcohols and modified polyvinyl alcohols which can be suitably used are described, for example, in Cline et al. U.S. Patent 2,636,803 and Osugi et al. Patent 2,906,594.

The copolymer of vinylidene cyanide and vinyl acetate is, as previously mentioned, an essentially 1:1 alternating copolymer and typical copolymers are described in Gilbert et al. U.S. Patent 2,615,866 as well as in Wootton et al. U.S. Patent 2,871,214.

The ratio between the polyvinyl alcohol and the VA–VC copoylmer may vary but suitably it ranges from 3:1 to 1:1 based on the weight of the polymers.

The polymeric spinning solution of this invention is spun in conventional manner by extruding the dimethylsulfoxide solution through small holes in a spinning jet into a medium effective to remove dimethyl sulfoxide therefrom. In wet spinning processes the medium can, for example, be acetone or the like or 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 the above-mentioned U.S. Patents 2,636,803 and 2,906,594.

The fibers are suitably stretched, heat treated and acetalized 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.

The 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.

The acetalization is conveniently carried out 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 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 the examples, all parts are by weight unless otherwise indicated.

Example 1

Polyvinyl alcohol having a degree of polymerization of 1760, and VA-VC copolymer of a degree of polymerization of 1500 were mixed in the ratio of 80% by weight of polyvinyl alcohol and 20% by weight of copolymer. Then the mixture was dissolved in dimethylsulfoxide to form a spinning solution containing 15% by weight of the polymer mixture.

This spinning solution was forced by compressed air through a spinneret having 100 holes into acetone. After spinning, the fibers were air-dried, stretched for 400% at 210° C. for 8 seconds, and formalized in conventional manner.

The thus produced and treated fibers were tested, with the following results:

There was no difference in strength as compared with ordinary vinylon but the elasticity of the fibers was greatly improved. Although the hot-water resistance was low, because the fibers had not been subjected to heat-treatment, the property of thermal stability was much better than ordinary vinylon. The following tables set forth the data obtained for the fibers:

Denier, d.	Strength, g./d.	Elongation, Percent	Young's Modulus, g./d.	Elasticity, Percent		
				1% Stretching	3% Stretching	5% Stretching
96.3	3.7	14.0	67	90	83	77

	Dry Heat, ° C.				Hot Water, ° C.		
	140	160	180	200	60	80	100
Thermal Stability, Percent	89	76	57	12	100	77	20

Example 2

The same spinning solution described in Example 1, was spun into methanol as the coagulating bath, the fibers stretched for 500% at 210° C. for 7 seconds and formalized in conventional manner. This yarn was then tested, with the following results:

Denier, d.	Strength, g./d.	Elongation, Percent	Young's Modulus, g./d.	Elasticity, Percent		
				1% Stretching	3% Stretching	5% Stretching
54.0	4.2	15.1	116	94	84	80

	Dry Heat, ° C.					Hot Water, ° C.		
	140	160	180	200	220	60	80	100
Thermal Stability, Percent	90	83	74	66	64	100	78	0

Example 3

A 10% dimethyl sulfoxide solution was prepared with polyvinyl alcohol of a degree of polymerization of 1750 and VA-VC copolymer of a degree of polymerization of 1050, the two polymers being mixed together to form a mixture in the weight ratio of polyvinyl alcohol to copolymer of 3. Some of the dimethyl sulfoxide was then evaporated away under reduced pressure until the concentration of the mixed polymer reached 16.5% by weight and the thus-formed spinning solution was spun in the manner described in Example 1, the fibers stretched for 400% at 235° C. for 5 seconds, and heat-treated at 240° C. for 5 seconds at a fixed yarn length. The various properties of the yarn after heat-treatment, and formalization are given below:

Denier, d.	Dry Strength, g./d.	Elongation, Percent	Wet Strength, g./d.	Elongation, Percent	Ratio of Dry-Wet Strength, Percent	Ratio of Knot Strength, Percent
2.00	3.02	23.2	1.98	32.3	66	100

Young's Modulus, g./d.	Elasticity, percent	
	3% Stretching	5% Stretching
71	62 (57)	54 (52)

AFTER FORMALIZATION

Denier, d.	Dry Strength, g./d.	Elongation, Percent	Young's Modulus, g./d.	Elasticity, percent	
				3% Stretching	5% Stretching
1.81	3.38	25.2	67	56 (46)	46 (46)

The determination of the coefficient of elasticity was effected in conventional manner and, for purposes of comparison, the values for pure polyvinyl alcohol fibers under identical conditions are given in parenthesis.

The strength of the fibers produced was somewhat lower than that of pure polyvinyl alcohol fibers, but it was fully sufficient, whereas the coefficient of elasticity was better. The elongation curve was very near that of pure polyvinyl alcohol fibers in form, but the Young's modulus was lower. The cross-section of the yarn was found to be homogeneous, and was nearly circular, but numerous small convex and concave areas were seen along the circumference. When the heat-treated and formalized yarn was dyed with direct dyes and Cellitone colors, it gave markedly deeper shades than did pure polyvinyl alcohol yarn.

Example 4

Using the method described in Example 3, a 15% dimethysulfoxide solution of polyvinyl alcohol and VA–VC copolymer in the weight ratio of 1:1 was prepared, and this solution was spun into fibers in the manner described in Example 1, using methanol as the coagulating bath. After natural-drying, the yarn was stretched 400% at 235° C. for 5 seconds, and heat-treated at 240° C. for 5 seconds at a fixed length.

Various properties of the yarn after heat-treatment and formalization were determined and are set forth below:

AFTER HEAT-TREATMENT

Denier, d.	Dry Strength, g./d.	Dry Elongation, percent	Wet Strength, g./d.	Wet Elongation, percent	Ratio of Dry-Wet Strength, percent	Ratio of Knot Strength, percent
1.06	2.37	23.2	1.52	46.4	63	84

Young's Modulus, g./d.	Elasticity, percent	
	3% Stretching	5% Stretching
53	71	58

AFTER FORMALIZATION

Denier, d.	Dry Strength, g./d.	Dry Elongation, Percent	Young's Modulus, g./d.	Elasticity, Percent	
				3 Percent Stretching	5 Percent Stretching
1.06	1.86	25.7	43	77	58

THERMAL STABILITY AFTER FORMALIZATION

	Dry Heat, ° C.				Hot Water ,° C.			
	140	160	180	200	70	80	90	100
Thermal Stability, Percent	90	75	30	0	96	93	86	78

As seen from the foregoing data, the strength was lower in comparison with pure polyvinyl alcohol but it was still higher than VA–VC copolymer fiber. On the other hand, the elasticity was greatly increased and thermal stability was improved. The yarn exhibited a dyeability as good as, or better than the yarn described in Example 3. The yarn was found to have a perfectly circular cross-section.

The conditions and the relative relationships set forth in the examples are those preferred in carrying out the process of this invention, but it will be understood that other conditions and relationships may be used within the scope of the invention. In general, unless otherwise indicated, conventional operations and techniques are suitably employed.

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.

I claim:

1. A spinning solution effective to be spun into fibers having high elasticity and dyeability which comprises dimethylsulfoxide having dissolved therein polyvinyl alcohol and a vinyl acetate-vinylidene cyanide copolymer, the weight ratio between said polyvinyl alcohol and said copolymer being within the range of from 1:1 to 3:1 based on the weight of said polymers, and said vinyl acetate-vinylidene cyanide copolymer being essentially a 1:1 alternating copolymer.

2. A spinning solution according to claim 1, wherein said vinyl acetate-vinylidene cyanide copolymer has a weight ratio of 1:1 of vinyl acetate and vinylidene cyanide.

3. A fiber having high elasticity and dyeability produced by spinning a solution composed of dimethyl sulfoxide having dissolved therein polyvinyl alcohol and a vinyl acetate-vinylidene cyanide copolymer, the weight ratio of said polyvinyl alcohol to said copolymer in said solution being within the range of from 1:1 to 3:1 based on the weight of said polymers, and said vinyl acetate-vinylidene cyanide copolymer being essentially a 1:1 alternating copolymer.

References Cited in the file of this patent

UNITED STATES PATENTS

2,146,295	Herrmann et al.	Feb. 7, 1939
2,589,294	Schmidt et al.	Mar. 18, 1952
2,615,866	Gilbert et al.	Oct. 28, 1952
2,636,803	Cline et al.	Apr. 28, 1953
2,682,518	Caldwell	June 29, 1954
2,682,519	Caldwell	June 29, 1954
2,779,746	Heisenberg et al.	Jan. 29, 1957
2,984,636	Lyman	May 16, 1961
3,080,350	Imai et al.	Mar. 5, 1963

FOREIGN PATENTS

809,346	Great Britain	Feb. 25, 1959