

UNITED STATES PATENT OFFICE

2,636,804

PROCESS OF TREATING POLYVINYL
ALCOHOL FIBERS

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No Drawing. Application February 4, 1950,
Serial No. 142,538

4 Claims. (Cl. 8—115.5)

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This invention relates to improved fibers of hydroxyl-containing polymers and, more particularly, to a process for their manufacture.

This application is a continuation-in-part of U. S. application Serial No. 656,538, filed March 22, 1946, now abandoned.

Fibers have previously been prepared from hydroxylated polymers such as polyvinyl alcohol or interpolymers such as those obtained upon hydrolysis of vinyl esters with small amounts of other polymerizable vinyl or vinylidene compounds. Filaments of these polymers can be oriented by drawing to yield fibers of high tensile strength. The fibers possess advantageous insolubility in organic solvents, such as those used in the dry cleaning industry. Furthermore, these hydroxylated polymers are high softening and fabrics produced therefrom usually are ironable when dry. Although fibers of such hydroxylated polymers exhibit the above advantages they have not found utility in the textile industry in view of their water sensitivity and their solubility in hot water. Polyvinyl alcohol as commercially produced is usually soluble in water at room temperature and fibers of such highly hydroxylated material when not under tension, retract and are either soluble or lose strength in water, particularly in warm water.

It is an object of this invention to provide fibers of oriented, hydroxyl-containing polymeric material of improved resistance to the deleterious effect of cold and hot water. Further objects reside in methods for obtaining these fibers by treatment of oriented fibers of hydrolyzed vinyl ester polymers.

The above objects are accomplished by the treatment described herein of oriented fibers of synthetic linear hydroxylated polymer having alcoholic hydroxyl groups on one half of the carbons of the polymeric chain. The present process involves shrinking the above described fibers at least 8% and not more than 60% of their oriented length and insolubilizing the fiber without shrinkage of more than a maximum of 60% of the original oriented length. In a preferred embodiment the shrunken fibers are swollen while held to prevent further shrinkage by contact with liquid aqueous medium until the fiber is substantially saturated directly before their insolubilization.

The shrinking can be effected by heat at, generally, 200–240° C. while the fibers are not under tension unless the shrinkage approaches 60%. The invention is conveniently practised by conducting the shrinking step with the aid of heat

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while the fiber is held in relaxed condition, and then holding the fiber to prohibit shrinkage more than 60% of the original length while contacting it with a swelling agent.

The invention in its best embodiment is carried out by the following procedure: In the first or shrinking step an oriented filament, by which is meant a filament of the above defined hydroxylated polymer that has been increased in length at least by 200% (draw ratio of 3/1) by drawing, is heated in relaxed condition to a temperature below the softening point of the polymer, usually 205–225° C., and at least above 180° C. until the fiber shrinks from 8% to 60% of its oriented length. It is preferable to first dry the fiber before heating. The exact temperature within the above mentioned range that is used in any instance will depend on the particular hydroxylated polymer composing the fiber, and also in methods used in its production, for example, whether it has been oriented by cold or by hot drawing.

In the second step the fiber is swollen by contact with water until the fiber is substantially saturated. This swelling, in which the fiber is at least 75% saturated with the treating liquid, can be effected by water alone or by aqueous swelling media containing at least 5% water, such as a mixture of water and alcohol. The amount of saturation of the fiber can be measured by noting the increase in cross-sectional area of the fiber. Complete saturation is achieved when the fiber has increased its maximum in cross-sectional area.

The insolubilization in the third step is effected by treatment with an aldehyde which is an insolubilizing agent for fibers of hydroxylated polymers. The insolubilization of this step may be conducted without further shrinkage of the fiber. In general the fiber is not held at fixed length unless excessive shrinkage tendency is noted.

The invention is further illustrated by the following examples in which the parts given are by weight.

Example I

An aqueous solution of polyvinyl alcohol was wet spun into an aqueous bath of 45% sodium dihydrogen phosphate. The coagulated yarn was stretched 3.66/1 between a Godet wheel and wind-up and the salt was removed from the yarn by washing the drawn yarn with water as described in U. S. Patent 2,474,617. The yarn after drying was stretched 2.5/1 in air at 225° C. and then relaxed 20% at 225° C., both stretching and relax-

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ing being carried out separately by a continuous process involving times of contact in the hot air of about 2-4 seconds.

The drawn and relaxed yarn was wound on a glass bobbin and immersed in water at 65° C. for ten minutes. The water was removed from the yarn by immersion in successive portions of fresh methanol. A treating solution was made by heating 600 parts of paraform, 600 parts of methanol and one part of 10% sodium hydroxide to give a clear solution. To this was added 97 parts of concentrated hydrochloric acid resulting in a bath consisting of 50 parts methanol, 50 parts formaldehyde and 2 parts hydrogen chloride. The methanol-wet yarn was soaked in this bath at 25° C. for 45 minutes. The treating solution was removed from the yarn by washing with fresh methanol. The treated yarn was washed with cold running water for 30 minutes and then was heated in water at 100° C. for ten minutes. After winding the yarn back off the bobbin it was found to shrink but 1.5% when immersed in water at 100° C. for five minutes. The dry tenacity was 6.2 g. per den. at 17% elongation, loop tenacity was 5.0 g. per den. at 15% elongation and wet tenacity was 5.2 g. per den. at 18% elongation. The elastic recovery from 4% stretch was 57%. After heating in water at 100° C. for 15 minutes this was reduced to 30%.

Example II

Polyvinyl alcohol yarn prepared by the same method as described in Example I and which had an initial dry tenacity of 6.4 g. per den. at 16.7% elongation was treated in the same manner as described in Example I except that isopropyl alcohol was substituted for methanol and the time of treatment in the isopropyl alcohol/formaldehyde/HCl (50/50/2) bath was varied with the results shown in following table:

Minutes in Treating Solution	Shrinkage after 5 minutes in water at 100° C.	Den.	Dry Tenacity	Elong., Percent	Elastic Recovery from 4-stretch
	Percent		G./den.		
40.....	1.5	61.5	4.5	13.7	49
90.....	2.5	62.0	3.8	11.5	52
180.....	3.2	62.9	4.2	12.6	57

Example III

A portion of the relaxed polyvinyl alcohol yarn described in Example I was wound on a glass bobbin, heated in water at 65° C. for 20 minutes, treated in a bath consisting of 360 parts formaldehyde, 7 parts hydrogen chloride and 645 parts water for 17 hours at 25° C., washed in running water for 30 minutes and boiled in water for ten minutes. The yarn on removal from the bobbin was found to shrink 5% in length on immersion in water at 100° C. for five minutes. It had a dry tenacity of 6.5 g. per den. at 16.8% elongation, a loop tenacity of 4.4 g. per den. at 12.7% elongation and a wet tenacity of 5.4 g. per den. at 18.8% elongation. Its elastic recovery from 4% stretch was 51%.

Example IV

A yarn spun from a commercial, medium viscosity grade of polyvinyl alcohol was drawn 2.4/1 at 225° C. and relaxed 20% at 225° C. as described in Example I. A skein of this yarn was heated in water at 75° C. for ten minutes during which less than an additional 5% shrinkage occurred. The skein of yarn was immersed in a treating

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bath consisting of 87 parts sodium bisulfate, 87 parts water, 10 parts formaldehyde and 18 parts sulfuric acid for 49 hours at 30° C. and then for an additional 15 hours at 65° C. The yarn was washed thoroughly in water and a dilute solution of sodium bicarbonate. The treated yarn had a dry tenacity of 4.8 g. per den. at 22% elongation and a modulus of 69 g. per den. It shrank 7% in water at 100° C. after six minutes. A sample of the treated yarn was heated in water at 100° C. for 15 minutes in skein form. The boiled yarn had a dry tenacity of 4.7 g. per den. at 30% elongation and a modulus of 56 g. per den.

Example V

An aqueous solution of polyvinyl alcohol was spun into a bath of 45% sodium/dihydrogen phosphate. The wet yarn was stretched 4.9/1 through a boiling 45% sodium dihydrogen phosphate solution. Salt was removed from the yarn by thorough washing with water and the yarn was dried. A skein of the dry yarn was heated in air at 215° C. for two minutes, during which the yarn shrank about 25%. The skein was then heated in water at 87° C. for ten minutes. The water in the skein was replaced by diethylene glycol and the yarn was heated for 90 minutes at 125° C. in a clear bath made by heating together two parts paraformaldehyde, 29 parts diethylene glycol and four parts phosphoric acid. The yarn was washed thoroughly in water containing a small amount of sodium bicarbonate. Increase in weight was 7%, equivalent to reaction with about 50% of the hydroxyl groups of the polyvinyl alcohol. The treated yarn had a sticking temperature of 212° C. It shrank 1.8% upon boiling in water for one hour. It had a dry tenacity of 2.0 g. per den. at 31% elongation after the boiling in water.

Example VI

Polyvinyl alcohol yarn prepared as described in Example V was treated in skein form in a bath composed of six parts of 3,5,5-trimethylhexanal, 58 parts of diethylene glycol and one part of ammonium chloride for 60 minutes at 125° C. After washing, the yarn was boiled one hour in water, during which it shrank 6.3%. The total shrinkage including that from baking in air through boiling in water was 36%. The weight gain was 30%. The yarn had a sticking temperature of 208° C., a dry tenacity of 2.0 g. per den. at 53% elongation and a modulus of 17 g. per den.

Example VII

The general procedure of Example VI was repeated except that the bath was composed of 16 parts of 2-n-propyl-2-heptenal, 58 parts diethylene glycol and 1 part ammonium chloride. It was heated 60 minutes at 135° C. Overall shrinkage that occurred amounted to 31%. The weight gain was 12%. The resultant yarn had a sticking temperature of 200° C., a dry tenacity of 2.6 g. per den. at 40% elongation and a modulus of 30 g. per den. The yarn did not shrink on boiling one hour in water.

Example VIII

Polyvinyl alcohol was spun and stretched 4.8/1 in the manner described in Example V. Skeins of the dry yarn were baked in air for two minutes at 215° C., then heated in water for ten minutes at 85° C. The water in the skeins was replaced with ethanol and the skeins were treated for 16 hours at 75° C. in baths made up of 20 parts of

ethanol containing phosphoric acid and one part each of the following aldehydes. The treated yarns were washed successively in ethanol and water and then boiled in water for one hour. Physical properties of the boiled yarns are shown in the table.

Aldehyde	H ₃ PO ₄ Parts	Shrinkage through Treatment, Percent	Wt. Gain, Percent	Shrinkage H ₂ O 100° C. 1 hr., Percent	Dry Ten., g. per den.	Elong., Percent	Modulus, g. per den.	Stick Temp., ° C.
n-Butyraldehyde.....	7	44	31	5.1	1.2	57	5	145
2-Methylbutyraldehyde.....	9	37	25	1.7	2.0	45	17	160
Isovaleraldehyde.....	7	41	32	3.3	1.2	43	10	180
n-Heptaldehyde.....	7	35	33	2.8	2.1	51	15	175
Hydrocinnamaldehyde.....	7	35	40	5.2	2.0	44	16	165

Wet spinning of fibers of polyvinyl alcohols for the above examples was carried out by spinning a 15% aqueous solution of the polymer into a saturated aqueous solution of NaH₂PO₄ at 25–60° C. and the filaments taken over a Godet wheel.

Considerable trouble has been previously encountered with removal of salts from polyvinyl alcohol fibers wet spun by this method in aqueous salt solutions. The fibers tend to dissolve or become tacky in water and attempts to remove the salts by washing with water result in fused filaments when the salt concentration in the filaments is low. In U. S. 2,388,325 it was shown that mixtures of water and organic solvents such as a 1:1 mixture of water and acetone can be employed to completely remove salts from polyvinyl alcohol structures freshly precipitated from aqueous inorganic salt solutions without injurious effect on the polyvinyl alcohol structure. If the salt laden fibers are drawn in air or at elevated temperatures to a ratio of from 2/1 to 5/1, sufficient water resistance is imparted to the fibers by this orientation that they can be washed free of salts without any injurious effects on the fibers, if the fibers are held at fixed length during the washing treatment as described in U. S. 2,474,617. The fiber is then dried, e. g., at 50° C. and further oriented by drawing in oil or air at 200–250° C. Alternatively and preferably the fibers may be stretched to a ratio of about 4.5/1 to 5.5/1 in 40–50% NaH₂PO₄ at about 100° C. followed by washing and drying.

Oriented fibers of macromolecular polyvinyl alcohol are employed in this invention. By "oriented fiber" is meant a fiber which has been drawn under tension to an extent such that it shows a typical fiber X-ray diffraction pattern showing a high degree of orientation. Fibers of this kind are obtained when filaments of the polymer are drawn at least 200% of the original length. The drawing can be effected in oil, air, or salt bath as described above although the specific technique for optimum results may vary with the particular fiber being employed. By this operation the length of the fiber is increased several times and the tensile strength correspondingly increased. By "macromolecular" is meant an organic compound having a degree of polymerization or a number of recurring units of at least 100 (Staudinger, *Die hochmolekularen organischen Verbindungen*, 1932).

In the first step of controlled relaxation of the oriented fiber 8% to 60% of its length, e. g., to a length which is from 92% to 40% of the length of the oriented fiber, the time required, which in some cases is less than one second, will depend on the temperature and the heating medium used. The fiber must be shrunk in this step within the

percentages just indicated. If shrinkage is allowed to proceed beyond 60% of the initial length, the fiber begins to lose its orientation and dissolves in hot water, or sticks together in other media. If on the other hand the treatment is not continued until about 8% shrinkage occurs,

the fiber after the aldehyde insolubilizing step will shrink excessively on contact with hot water.

The second step, swelling the fiber at fixed length prior to insolubilization, facilitates the insolubilization of the fiber. Omission of this step results in a poorer quality product.

In the second step, in which the fiber is swollen with water while shrinkage more than the maximum of 60% of the original oriented length is prevented, temperatures of from 60° C. to 100° C. can be used. At lower temperatures the time required for penetration of the liquid to produce swelling will be longer than at the higher temperatures where the time is usually 2 to 10 minutes but will depend on the size of the yarn package and the temperature at which the fiber tends to dissolve.

The insolubilizing agents most useful for the present purpose are those aldehydes which can be used in aqueous solution, and of these formaldehyde is particularly valuable. The examples illustrate various other aldehydes that can be used. In general, the aldehydes most useful are the non-aromatic aldehydes and of these aliphatic aldehydes and particularly the alkanals of 1 to 10 carbons are preferred. In the case of formaldehyde either an aqueous solution of formaldehyde, or a solution of material which yields formaldehyde on heating can be used. In general, the insolubilizing reaction is readily effected at temperatures of 0 to 150° C., one means is by heating the filament containing the formaldehyde at 55–150° C. in the presence of a relatively small amount (1–10% based on the weight of formaldehyde present) of an acid catalyst such as oxalic acid, ammonium chloride, or phosphoric acid. After baking the filaments can be washed and heat-set.

The formaldehyde-treated fibers shrink to an extent of usually more than 50% when heated to a temperature as high as the melting point of the original untreated polymer. The fibers thus can be ironed safely. It has been found that heating the formaldehyde-treated fibers while held at fixed length to temperatures of 20–50° C. above the melting point of the original polymer gives fibers which shrink only 5–10% when heated to a temperature of 5° below the heat setting temperature employed. Thus fibers are obtained which can be ironed safely at temperatures of 15–45° C. above the melting point of the original polymer.

The treated fibers obtained in accordance with the process described herein withstand boiling water in which they in general show a shrinkage of but 2–6% or less and have a tenacity while wet of 80–90% of the dry tenacity. Because of these high wet strengths inherent resistance of

the highly hydroxylated polymers to organic solvents and to heat, these fibers are useful for the production of fabrics, hosiery, cordage, etc.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. A method for improving the water insensitivity of polyvinyl alcohol fibers having alcoholic hydroxyl groups on one half of the carbons of the polymeric chain, said process comprising heating in relaxed condition an oriented fiber of said polymer to a temperature of from 180° C. to 225° C., allowing the fiber to shrink during said heating, continuing said heating until the fiber shrinks from 8% to 60% of its oriented length, swelling the shrunken fiber by contacting it, while preventing shrinkage beyond 60% of the original oriented length, with inert liquid aqueous medium containing at least 5% water and selected from the class consisting of water and aqueous alcohol until the fiber is substantially saturated, and insolubilizing the fiber, while preventing shrinkage beyond said 60%, by impregnating with an aldehyde, in solution, at a temperature of 0-150° C. in the presence of an acid catalyst.

2. A method for improving the water insensitivity of polyvinyl alcohol fibers having alcoholic hydroxyl groups on one half of the carbons of the polymeric chain, said process comprising heating an oriented fiber of said polymer in relaxed con-

dition to a temperature of from 180° C. to 225° C., allowing the fiber to shrink during said heating, continuing said heating until the fiber shrinks from 8% to 60% of its oriented length, swelling the shrunken fiber by contacting it while held at fixed length with inert liquid aqueous medium containing at least 5% water and selected from the class consisting of water and aqueous alcohol until the fiber is substantially saturated, and insolubilizing the fiber while preventing a shrinkage beyond said 60% of the original oriented length by impregnating with an aliphatic aldehyde, in solution, at a temperature of 0-150° C. in the presence of an acid catalyst.

3. The process set forth in claim 2 in which the swollen fiber is insolubilized by impregnating it with formaldehyde.

4. The process set forth in claim 2 in which the swollen fiber is insolubilized by impregnating it with formaldehyde at 55-150° C.

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