June 27, 1961 TSUKUMO TOMONARI ET AL 2,990,235

PROCESS OF IMPROVING THE HEAT AND WATER RESISTANCE OF POLYVINYL ALCOHOL FIBERS WITH LOWER ALIPHATIC ALCOHOL VAPORS OR SUPERHEATED STEAM AND OPTIONALLY ACETALIZING SAID FIBERS

Filed July 23, 1952 4 Sheets-Sheet 1

Fig. 1

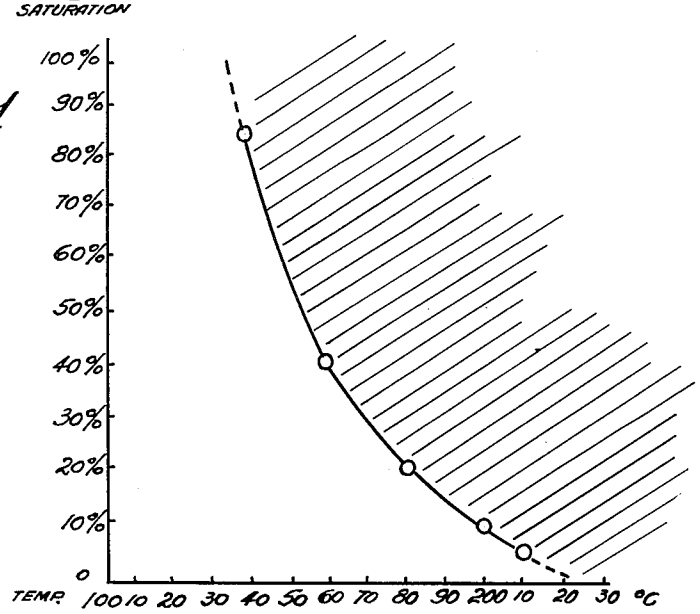
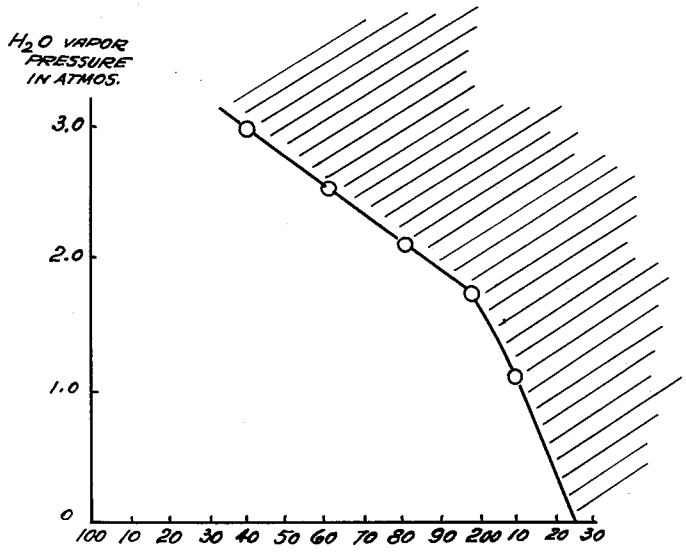


Fig. 2



INVENTOR.
TSUKUMO TOMONARY
SHIGEKI NOMURA

BY Fritz G. Hohwald

AGENT

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Fig. 3

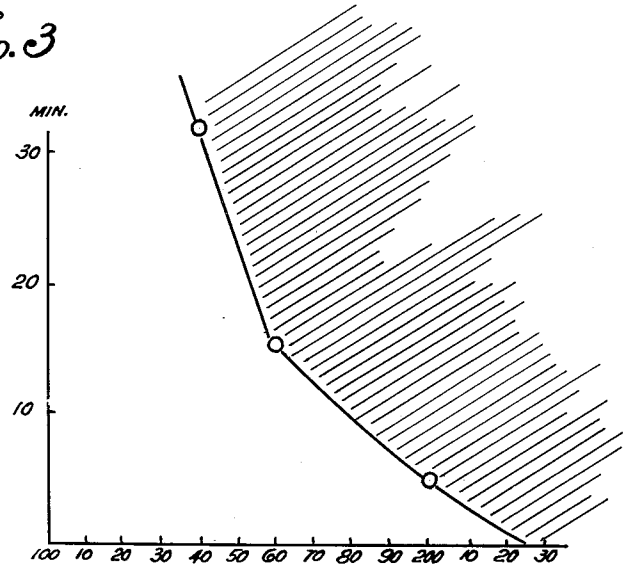
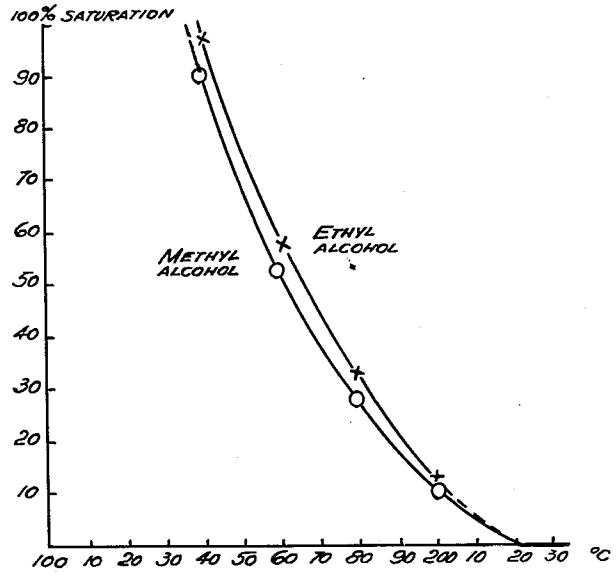


Fig. 4



INVENTOR
TSUKUMO TOMONARI
SHIGEKI NOMURA

BY Zeiz C. Hurlbut

AGENT

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Fig. 5

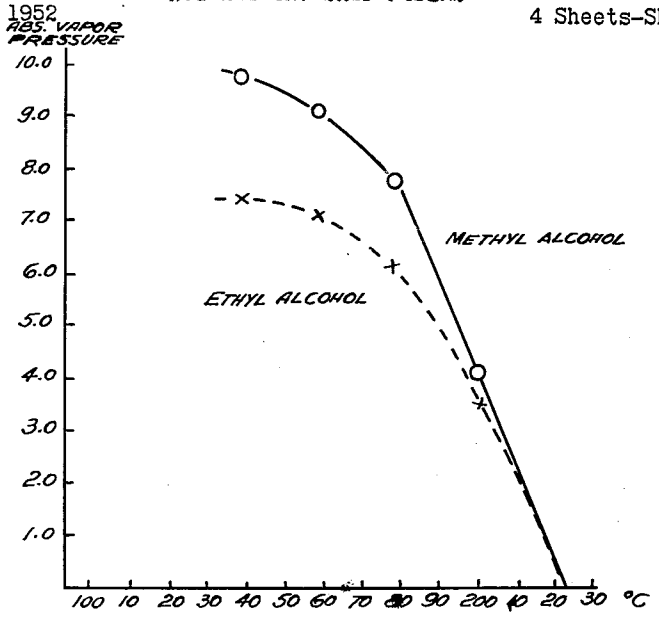
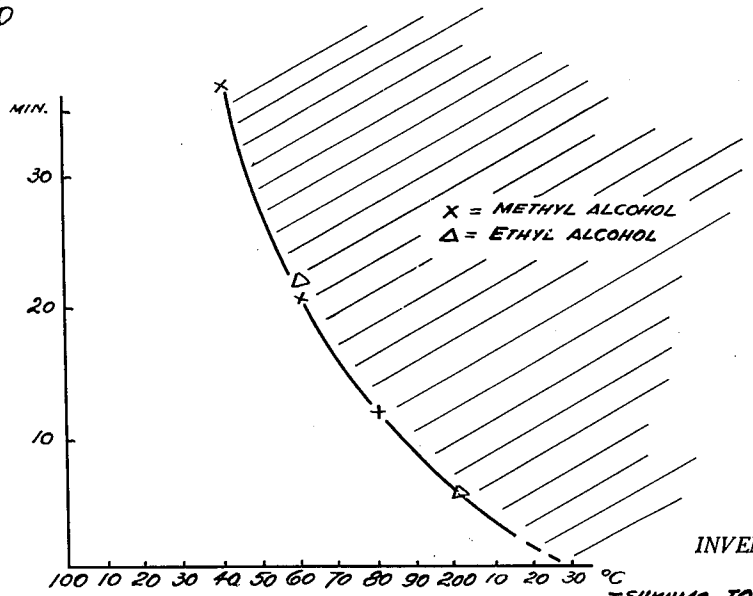


Fig. 6



INVENTOR.

BY TSUKUMO TOMONARI
SHIGEKI NOMURA

Fritz G. Hohwald

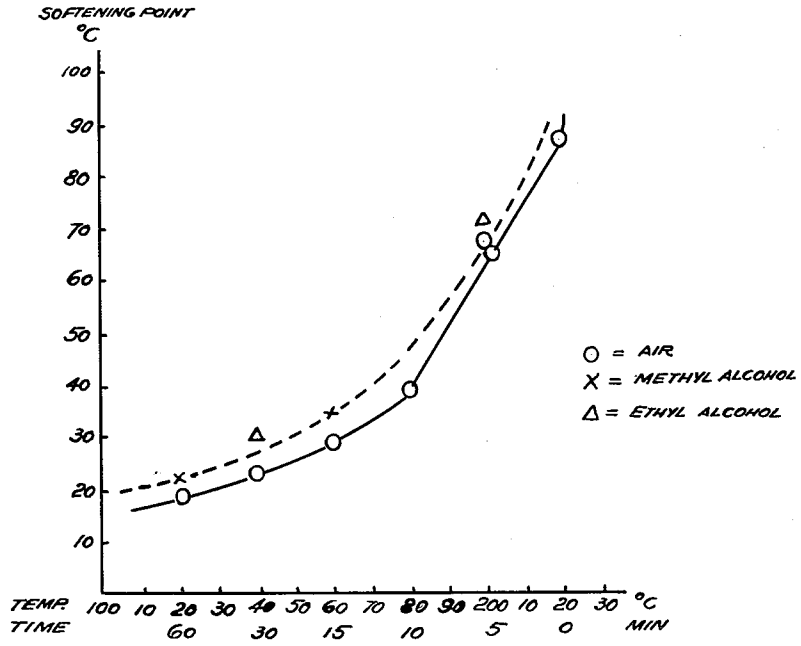
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Filed July 23, 1952 4 Sheets-Sheet 4

Fig. 1



INVENTOR.
TSUKUMO TOMONARI
SHIGEKI NOMURA

BY Fritz G. Hohnel

AGENT

United States Patent Office 2,990,235 Patented June 27, 1961

2,990,235

PROCESS OF IMPROVING THE HEAT AND WATER RESISTANCE OF POLYVINYL ALCOHOL FIBERS WITH LOWER ALIPHATIC ALCOHOL VAPORS OR SUPERHEATED STEAM AND OPTIONALLY ACETALIZING SAID FIBERS

Tsukumo Tomonari, Osaka, and Shigeki Nomura, Kurashiki, Japan; Tatsuko Tomonari and Natsuko Tomonari, heirs of said Tsukumo Tomonari, deceased, assignors, by direct and mesne assignments, of one-fourth to Air Reduction Company, Incorporated, New York, N.Y., a corporation of New York, and three-fourths to Kurashiki Rayon Co., Ltd., Okayama Prefecture, Japan, a corporation of Japan

Filed July 23, 1952, Ser. No. 300,375
Claims priority, application Japan May 18, 1949
4 Claims. (Cl. 18—54)

This application is a continuation-in-part of our copending application, Serial No. 154,873, filed April 8, 1950, now abandoned.

The invention relates to a process for increasing the heat resistance, particularly the wet heat resistance, and improving the elastic and other properties of polyvinyl alcohol fibers.

It is known to dry spin aqueous polyvinyl alcohol solutions in dry air or other gases at temperatures ranging from room temperature upwardly to 100–160° C. and to accelerate the drying by supplying hygroscopic vapors to the drying chamber. This treatment is said to prevent deformation of the thread in unwinding, but it does not increase the water resistance of the obtained fibers.

If such fibers are subsequently treated with formaldehyde, their water resistance is increased, but they still show such a high shrinkage in boiling water as to make it impossible to use such fibers for normal textile purposes. Such threads were useful only for surgical purposes where their ready absorption by the body liquids is an advantage.

Another method of improving the water resistance of polyvinyl alcohol filaments consisted in acetalizing polyvinyl alcohol filaments at elevated temperatures in a highly stretched state. The filaments thus obtained were said to shrink only about 1% in length when immersed in boiling water for one minute and to have good resilience. However, these highly acetalized fibers have a relatively low softening temperature and are not water resistant when subjected to boiling water for longer times, and as they are acetalized in highly stretched state, they have hardly any elongation properties. They are, therefore, useful only for the manufacture of bristles and similar unelastic structures and cannot be used as substitutes for textile fibers in the manufacture of textile goods, where high water resistance and good elongation and recovery properties are of primary importance.

Although polyvinyl alcohol is a cheap and readily available starting material, and although it has been known for many years that polyvinyl alcohol can be spun into filaments, the above recited shortcomings of the known polyvinyl alcohol fibers explain that polyvinyl alcohol fibers have, heretofore, never been used in commerce as substitutes for the conventional natural or synthetic fibers in textile goods.

It is a principal object of the invention to provide a method for imparting improved heat resistance and good elastic properties to polyvinyl alcohol fibers so as to render them suitable for the manufacture of textile goods.

Another object of the invention is to provide a method for improving the water resistance of polyvinyl alcohol fibers without impairing their heat resistance and their elastic properties.

Other objects and advantages will become apparent from a consideration of the specification and claims.

We have discovered that by drying wet fibers obtained in the wet spinning process and by subsequently subjecting said dried fibers to a heat treatment at elevated temperatures up to close to the melting point of the polyvinyl alcohol, the softening temperature of the fibers can be substantially increased and that such fibers, when subsequently partially acetalized, have such a high heat and water resistance that they shrink very little in boiling water even when immersed therein for extended periods of time. This low shrinkage combined with excellent elongation properties, making the fibers an excellent material for manufacturing textile goods of the most diverse kinds.

In the course of our extensive investigations, we have found that in order to obtain polyvinyl alcohol filaments which are suitable for textile purposes, these filaments must have, before acetalization, a softening point in water of at least 80° C. We designate as softening point the temperature at which the filaments shrink by 5 percent of their length. According to the invention, the following conditions have to be maintained to obtain fibers having such a high softening point.

(1) The fibers which are spun from an aqueous polyvinyl alcohol solution by the wet spinning process, preferably using a slightly acid coagulating bath, are dried at temperatures not exceeding 160° C. and the drying operation has to be so adjusted as to avoid damage of the fibers by a too-sudden evaporation of the water adsorbed.

The fibers may be dried in the unstretched or stretched state. In the former case, relatively lower drying temperatures have to be applied to avoid shrinkage of the fibers. We prefer to dry the fibers immediately following the spinning step while under stretch, whereby further drawing should be avoided or at least limited to an elongation of the fibers not exceeding 10 percent. In this case, higher temperatures, within the recited temperature range, may be employed.

The temperatures given relate to the temperature of the drying medium, which is preferably air or another chemically inert gas, such as nitrogen.

If the temperature is raised above 160° C. before the moisture content is reduced to less than 10 percent, preferably less than 4 percent, the fibers are weakened by swelling and subsequent uneven shrinkage.

Though high drying temperatures close to 160° C. obviously shorten the drying time, we prefer to use lower temperatures and longer drying times to prevent any risk of a softening and shrinking of the wet fibers.

(2) The dried fibers, i.e. fibers containing less than 10 and preferably less than 4% moisture are then subjected to a heat treatment with superheated steam and/or vapors of water soluble lower aliphatic alcohols at temperatures exceeding 135° C. up to close to the melting point of the fiber, whereby at temperatures from 135° to about 200–210° C. inversely increasing pressures up to about 10 at. have to be used. When superheated steam is used, we found that the degree of saturation, together with the temperature and pressure, are the governing factors which influence the outcome of the heat treatment. The higher the degree of saturation, the lower is the temperature, and under such conditions the time of treatment must be accordingly prolonged. FIGURE 1 illustrates the relationship of the minimum temperature and the minimum degree of saturation for water vapor for obtaining a fiber which has, after the treatment, a minimum softening point of 80–85° C. in water.

FIGURE 2 shows the relationship of the vapor pressure against the temperature and here again the lower temperature corresponds to the higher pressure to obtain the softening point of 80–85° C. which we consider the

minimum softening point for a satisfactory fiber as obtained after acetalization.

FIGURE 3 shows the relationship between heating time and temperature, and here too it is obvious that the lower the temperature, the longer the heating time.

An analysis of these three curves shows that in order to obtain a softening point of 80–85° C. of the fiber the heat treatment must be carried out along the curves or in the shaded areas of the graphs. It further shows that the same final result can be obtained by heat treatment, for example, at 135° C. at 85% saturation and 3 atm. pressure for 30 minutes or at 210° C. at 6% saturation and 1.1 atm. pressure for three minutes; however, an 80° C. softening point cannot be achieved when the fiber is heated under conditions falling below the curves in regard to the saturation degree, pressure and heating time. The optimum heating time, pressure and temperature will, of course, depend to a certain degree on the denier of the filament spun, the degree of polymerization of the polyvinyl alcohol used and also on the spinning conditions, degree of orientation, and other factors.

We further found that a heat treatment in the vapors of water soluble lower aliphatic alcohols such as methanol, ethanol, isopropanol, sec. butanol, tert. butyl alcohol, allyl alcohol, improves the softening point of the fiber to the desired degree if conditions are maintained as illustrated in FIGS. 4 to 6.

FIG. 4 shows the relationship between the degree of saturation of methyl alcohol and ethyl alcohol vapors against the temperature for increasing the softening point of the treated polyvinyl alcohol fiber to 80–85° C. It is seen that below 140° C. corresponding to 100% saturation, the softening point cannot be raised enough. By increasing the temperature the saturation can be reduced to 14% at 200° C. to obtain the desired effect.

FIG. 5 shows the relationship of the pressure and temperature to the desired increase of the softening point to 80–85° C.

FIG. 6 shows the relationship of heating time to temperature for the same desired softening point of 80–85° C. It is demonstrated that below the shaded area the desired effect cannot be obtained.

FIG. 7 shows the relationship of the softening point of the heat treated fiber and the temperature and time of the heat treatment in air, methyl alcohol, and ethyl alcohol at ordinary pressure of 1 atm. The curve shows that at atmospheric pressure the high softening point of 80–85° C. which we found necessary cannot be obtained at lower temperature than 210° C. However, if the heat treatment is carried out at this temperature in air, a yellow to brown fiber is obtained which is not suitable for normal textile use. The heat treatment at 210° C. in superheated steam or alcohol vapors does not produce any discoloration. At temperatures below 210° C., it is impossible to increase under any conditions the softening point to 80–85° C. by a treatment in air, whereas such increase is readily obtained in superheated steam or alcohol vapors under the conditions set forth hereinbefore.

Saturated steam cannot be used as a heating medium because dewdrops will form on the filaments, which will then weaken, swell and stick together.

Heating in air increases the softening point sufficiently only at temperatures above 210° C. and produces discoloration, as stated above.

If the heat treatment with superheated steam or alcohol vapors is applied before the fibers are sufficiently dried, they are weakened by the sudden and uneven evaporation of their moisture content and cannot be used for textile purposes.

This heat treatment with superheated steam or alcohol vapors increases the water resistance of the polyvinyl alcohol fibers to an extraordinary degree. The softening point is raised from about 15–45° C. of the dried fiber to at least 80° C. of the after-treated fiber. As already stated, we have found that polyvinyl alcohol fibers must have such a high softening point in order to assume after acetalization a sufficient resistance to boiling water.

In order to increase further the water resistance of the heat-treated fibers, they are then partially acetalized by reacting them with an aqueous solution of a suitable mono or dialdehyde, for instance formaldehyde, acetaldehyde, glyoxal or similar aldehydes. This acetalization should not acetalize more than about 50 percent of the hydroxyl group originally present in the polyvinyl alcohol molecules because otherwise the fibers would assume the low melting point and low elasticity of acetal resins, which properties are unsuitable for textile fibers. A partial acetalization with formaldehyde acts particularly in the direction of improving the mechanical strength of the fibers, whereas a treatment with glyoxal improves particularly the water resistance and raises the temperature at which textiles made from such fibers can be ironed without damage.

We believe that we can offer an explanation for the superior properties of the fibers treated in accordance with our invention, though we do not wish to limit the scope of our invention in any way by such explanation.

It appears that the heat treatment of the dried fibers with superheated steam or alcohol vapors produces at least three different simultaneous or consecutive changes in the polyvinyl alcohol chain.

These changes may be defined as a removal of chemically bound water with internal ether formation, secondly as an oxidation of secondary alcohol groups to carbonyl groups which in turn react with free hydroxyl groups to form inner acetals and semiacetals as well as ketals and semiketals, and last as a formation of hydrogen bonds which contribute to a tighter packing of the polymer chain.

Fibers produced by a wet stretch-spinning process are not uniform but depending on the degree of stretch orientation and the method of stretching, they contain amorphous as well as crystalline regions. In the crystalline or oriented regions the packing of the molecules is much tighter than in the unoriented or amorphous regions, because the hydroxyl groups of the polyvinyl alcohol in the amorphous part are more reactive; these hydroxyl groups are not hindered as the hydroxyl groups in the tighter packed crystalline regions are. The ratio of crystalline to amorphous region per unit cross section determines to a large extent the physical properties of the fiber, the higher the ratio of the crystalline part the more water resistant is the fiber. If means will be found to increase the crystalline part of the fiber to a much larger degree than possible at present, a fiber could be produced which will stand boiling water and even higher temperatures and an acetalization of such a fiber could be omitted. The ratio of these hindered hydroxyl groups to the total available OH groups depends on a number of factors such as the molecular weight and purity of the polyvinyl alcohol used, the degree of orientation, degree of cross-linking by inner acetal and ketal formation, the denier and the ratio of the crystalline to amorphous part. We found that by the heat treatment according to our method about 10–20% of the total OH groups available in the initial polyvinyl alcohol are hindered and bound by intramolecular and intermolecular hydrogen, acetal, semiacetal, ketal and semiketal bonds; additional 30—40% of the original OH groups are acetalized during the subsequent acetalization step, so that about 40–60% of the initial free OH groups remain in the finished fiber.

Therefore, it appears that the particular effect of superheated steam and alcohol vapors in our process cannot be explained merely by their good heat transfer properties but that the chemical affinity of the hydroxyl compounds to the polyvinyl alcohol promotes the aforementioned reactions. It appears further that all these

reactions are catalyzed by the presence of small amounts of aldehydes and particularly by mineral acids, and we prefer to carry out our process with fibers obtained by coagulation in an acid bath and by applying the heat treatment immediately following the spinning step, where the fibers still contain absorbed small amounts of the acid from the coagulating bath.

Polyvinyl alcohol fibers dried below 160° C. and acetalized without a previous heat treatment according to the invention have insufficient water resistance. It is true that the polyvinyl alcohol molecules in such fibers can be oriented by strong stretching during acetalization and fixed in their position, but the acetal thus formed has either low heat resistance when the acetalization degree is high, or low wet-heat resistance when the acetalization degree is low.

The following examples are given to illustrate the process of the invention but are not to be considered as limiting our invention in any way.

Example 1

A 14.0 percent aqueous solution of polyvinyl alcohol having an average degree of polymerization of 1600 is is extruded through a spinneret having 2,000 holes of 0.08 mm. diameter into a coagulating bath containing 390 g. of sodium sulphate per liter and 0.2 percent of sulphuric acid. The extruded and coagulated tow is stretched in the spinning bath and removed continuously over godet rollers. The tow is then dried for about 2–4 min. at a temperature below 160° C. until its moisture content is below 10 percent and then subjected to a heat treatment by passing the tow continuously through a chamber heated to 220° C. with superheated steam of 1 atm. having a saturation degree of 5.2%. The time of treatment is about 3 minutes. The softening point in water of the thus treated tow is raised from 15° C. to 85° C. The heat-treated fiber is then acetalized in a bath consisting of 15 percent of H_2SO_4, 15 percent of Na_2SO_4, and 5 percent of formaldehyde at 60° C. for 60 minutes, washed and finished. The filament obtained has the following physical characteristics.

Denier	2.03
Dry tensile strength	3.96 g./d.
Wet tensile strength	3.50 g./d.
Dry elongation	17.4%
Wet elongation	18.0%
Shrinkage in water at 100° C	1.8%
Degree of acetalization	35%
Color	White

If an identically coagulated and dried tow is heat-treated in air at 220° C. for 3 minutes and then acetalized in the same acetalizing bath, the obtained fiber is yellowish brown and the physical properties of the fiber vary over a wide range, showing unevenness of the individual filaments.

Example 2

A 14.8 percent aqueous solution of polyvinyl alcohol having a polymerization degree of 1800 is extruded through a spinneret having 1700 holes of 0.06 mm. diameter into a coagulating bath containing a small amount of acid. The coagulated fibers are stretched in the bath and continuously removed over a godet roller and dried for a few minutes in stretched state at 140° C. until the moisture content is less than 10%. The filaments are then placed in a chamber and treated therein at 4.6 atm. for 30 min. at 160° C. with methyl alcohol vapor having a saturation degree of 75%. The softening point of this fiber is 82° C. The tow is then acetalized in a bath consisting of 15 percent of H_2SO_4, 15 percent of Na_2SO_4 and 5 percent of formaldehyde at 50° C. for 1 hour. The physical properties of the fiber are:

Denier	2.56
Dry tensile strength	3.50 g./d.
Dry elongation	16.6%
Wet tensile strength	2.96 g./d.
Wet elongation	16.8%
Shrinkage in water at 100° C	2.8%
Color	White
Degree of acetalization	33%

An identical fiber which after drying is heat treated in air for 30 minutes at 160° C. has a softening point of only 40° C., and after acetalization in the same acetalizing bath a shrinkage of 55 percent in boiling water, and on longer contact with boiling water it melts and forms a ball.

Example 3

A 14.0 percent aqueous solution of polyvinyl alcohol having a polymerization degree of 1900 was extruded through a spinneret having 2,000 holes into a coagulating bath containing mineral acid. The coagulated bundle of fibers is stretched in the coagulating bath, removed over godet rollers and dried in the stretched state at a temperature below 160° C. until the moisture content is about 5 percent, which takes about 2–3 min. The dried multifilament yarn, which at this point is still completely soluble in water, is passed within 10 min. through a chamber which is heated with superheated steam of a pressure of 2.4 atm. having a saturation degree of 13% and a temperature of 200° C. The filament which leaves the chamber after this heat treatment has a softening point of 84° C. The same multifilament yarn when heated at 200° C. in air for 10 minutes has a softening point of 75° C. Both multifilament fibers are then simultaneously treated in an acetalizing bath for 60 minutes at 60° C. consisting of 15 percent of H_2SO_4, 15 percent of Na_2SO_4 and 5 percent of formaldehyde. The fiber which was heated in air shrinks considerably in the acetalizing bath and the acetalizing must be performed in stretched state, whereas the fiber heat-treated in steam does not shrink appreciably in the acetalizing bath. The acetalized fibers are then finished by washing, oiling, and drying. The fiber heated in superheated steam has the following physical characteristics:

Denier	5.05
Dry tensile strength	2.86 g./d.
Dry elongation	18.5%
Wet tensile strength	2.45 g./d.
Wet elongation	20.4%
Shrinkage in water at 100° C	2.0%
Degree of acetalization	34%
Color	White

The air-heated fiber is yellowish; the results are erratic and the physical constants show so large variations from test to test as to make it impossible to give sound averages. The produced fiber is too uneven to be suitable for commercial use.

Example 4

A multifilament tow as obtained according to Example 1 was, after spinning, dried at 110° C. for about 3–5 min. until the moisture content was less than 5%. The dried tow was cut on a fiber cutter to staple fibers and subjected for 10 min. to a heat treatment in superheated steam of 2.5 atm., having a saturation degree of 25% and a temperature of 180° C. The staple fiber acquired a fine and even crimp during the heat treatment, and the softening point was raised to 82° C. The thus treated staple fiber was then soaked in an acetalizing bath as

described in Example 1. The finished staple fiber had the following physical characteristics:

Denier	3.03
Dry tensile strength	3.06 g./d.
Dry elongation	18.7%
Wet tensile strength	2.40 g./d.
Wet elongation	20.2%
Shrinkage in water at 100° C.	2.2%
No. of crimps	25/inch

Example 5

The dried tow as obtained according to Example 1 was subjected to a heat treatment in the vapor of ethyl alcohol at 160° C. for 20 minutes. The alcohol content of the heating medium was 65%, and the vapor pressure was 8 atm. The softening point of the treated fiber was raised to 86° C. The thus treated fiber was then soaked in an acetalizing bath as described in Example 1. The shrinkage of the obtained fiber in water at 100° C. was only 1.8%. When the same tow was treated in the vapor of ethyl alcohol at 60° C. at 1 atm. pressure, the softening point of the treated fiber was 37° C. and that of the acetalized fiber 56° C.

Example 6

The dried staple fiber as obtained according to Example 4 was subjected to a heat treatment in methyl alcohol vapor at 140° C. for 1 hour. The alcohol content of the heating medium was 96% and the vapor pressure was 10.3 atm. The staple fiber acquired a fine and even crimp and the softening point was raised to 83° C. The treated fiber was then soaked in an acetalizing bath containing 22% H_2SO_4, 27% Na_2SO_4 and 0.5% glyoxal, at 70° C. for 1 hour. The obtained fiber did not shrink in boiling water and had a softening point of 225° C. in air.

Example 7

The dried tow as obtained according to Example 1 was subjected to a heat treatment in ethyl alcohol vapor at 180° C. for 15 minutes. The alcohol content of the heating medium was 36% and the vapor pressure was 7 atm. The softening point in water of the thus treated tow was raised to 84° C. The heat treated fiber was then soaked in an acetalizing bath containing 22% H_2SO_4, 27% Na_2SO_4, 0.5% glyoxal, 1% formaldehye at 70° C. for an hour. The obtained fiber had excellent water and heat resistance and properties similar to the fiber described in Example 6.

It is to be understood that details of our process given in the examples are only by way of illustration and that variations may be made without departing from the spirit of the invention. For instance, we can combine the tows of several spinning units and pass those combined tows through the drying and steaming installation, in which case the drying and heating times will be somewhat longer than indicated in the examples.

What we claim is:

1. A process for improving the heat and water resistance of polyvinyl alcohol fibers by a heat treatment not producing discoloration, which process comprises heating polyvinyl alcohol fibers containing not more than 10 percent of water in the vapor of a compound selected from the group consisting of superheated steam and water soluble lower aliphatic alcohols, at about 140 to 225° C. for about 60 to 3 minutes, the longer periods of time being employed at the lower temperatures, the minimum pressure of said vapors varying inversely as the temperature from about 1 atm. at 225° C., to about 4 atm. at 140° C. for said superheated steam, and to about 8 atm. at 140° C. for said lower aliphatic alcohols.

2. The process as defined in claim 1, wherein said fibers are subsequently acetalized in a bath containing an aldehyde selected from the group consisting of formaldehyde, acetaldehyde and glyoxal, and removed from said bath after about 30 to not more than 50 percent of the hydroxyl groups present in the initial fiber are acetalized.

3. A process for improving the heat and water resistance of polyvinyl alcohol fibers comprising the steps of extruding an aqueous solution of polyvinyl alcohol into an acid coagulating bath to form filaments of polyvinyl alcohol, drying said filaments in a chemically inert gas at temperatures below 160° C. to a water content below about 5 percent and heating said dried filaments, while still containing adhered thereto acid from said coagulating bath, in the vapor of a compound selected from the group consisting of superheated steam and water soluble lower aliphatic water soluble alcohols at about 140 to 225° C. for about 60 to 3 min., the longer times being employed at the lower temperatures, the minimum vapor pressure of the superheated steam varying inversely as the temperature within the range of about 1 atm. for about 225° C. to about 4 atm. at 140° C., the minimum vapor pressure of said alcohols varying within the range of about 1 atm. for about 225° C. to about 8 atm. at 140° C.

4. The process as defined in claim 3 wherein said filaments are dried in the stretched state.

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