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POLYVINYL ALCOHOL FIBERS AND
PROCESS OF TREATING

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This invention relates to improved synthetic fibers. More particularly it relates to the treatment of oriented polyvinyl alcohol fibers to obtain fibers having outstanding resilience and resistance to boiling water, and to a process for preparing these fibers.

It is known that filaments of hydroxylated polymers such as polyvinyl alcohol or hydrolyzed copolymers of vinyl esters with minor amounts of polymerizable vinyl or vinylidene compounds can be oriented by drawing to yield fibers of high tensile strength. These oriented fibers have many important advantages such as insolubility in most organic solvents and high softening point. However, they are characterized by undesirable sensitivity to water, particularly hot water. Moreover, these fibers lack the resilience necessary for the production of satisfactory fabrics. This latter disadvantage is observed even with fibers of hydroxylated polymers which have been treated so as to decrease or eliminate water sensitivity, either chemically, as described in application Ser. No. 142,538, filed by McClellan and Stevenson on February 4, 1950, as a continuation-in-part of application Ser. No. 656,538, filed March 22, 1946, the earlier being now abandoned or physically, as described in application Ser. No. 157,634, filed April 22, 1950, now Patent Number 2,610,360 as a continuation-in-part of application Ser. No. 19,444, filed by Cline, Pinkney, Plambeck and Stevenson on April 6, 1948, now abandoned.

It has been proposed to treat polyvinyl alcohol fibers with aldehydes such as formaldehyde, butyraldehyde or crotonaldehyde for various purposes. When such treatments are carried out to as near completion as possible, there results a completely or substantially completely acetalized product which no longer possesses the properties of polyvinyl alcohol, in that it has a much lower softening point and the fibers cannot be stabilized against shrinkage in boiling water if oriented to improve strength. When the reaction is only partial, the products heretofore described have been characterized by low work recovery in the fiber form and, in fabrics, by poor resilience characteristics such as crease resistance and recovery from crease.

Attempts have also been made to produce resilient polyvinyl alcohol fibers by partial acetalization of the polyvinyl alcohol in bulk form with cyclic aldehydes such as benzaldehyde, followed by spinning the partial polyvinyl acetal from an organic solution and stretching the fiber. However, it has been found that the oriented

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fibers so obtained shrink very badly in boiling water. Moreover, attempts to apply to these fibers a heat treatment to reduce their shrinking tendencies fail because the fibers stick at the required temperature, or, if the temperature is lowered, the excessive shrinkage in water is not prevented. Even a formaldehyde treatment does not give adequate water resistance to fibers obtained by spinning partial acetals of polyvinyl alcohol with cyclic aldehydes.

This invention has as an object the preparation of synthetic fibers of outstanding resistance to hot water and insolubility in most organic solvents, of high softening point and tensile strength, of high work recovery in fiber form and good resilience characteristics in fabric form, and of satisfactory shrink resistance on treatment with hot water. Another object is the treatment of oriented polyvinyl alcohol fibers to obtain fibers of outstanding resilience and outstanding resistance to hot water. Other objects will appear hereinafter.

These objects are accomplished by this invention wherein filaments of a synthetic linear polymer having hydroxyl groups directly attached to the carbon chain of the polymer, said polymer consisting, to the extent of at least 90% by weight, of vinyl alcohol, $-\text{CH}_2\text{CHOH}-$, units, i. e., a polyvinyl alcohol polymer in which 45-50% of the carbon atoms of the polymer chain are attached to hydroxyl groups, are subjected to a treatment comprising (1) heating the oriented fibers in the dry state, i. e., free from water, under tensions between that causing zero shrinkage and that causing 60% shrinkage, i. e., in a substantially anhydrous, nonsolvent fluid medium to a temperature from 1° to 30° C. lower than the softening point of the fiber (the point at which filament sticking occurs), the heating being carried out under conditions permitting the fiber to shrink from 0% to 60% of its initial drawn length, until a fiber is obtained which shrinks not more than 10% of its length when immersed in water at 60° C. and dried, and continuing the heating before appreciable color develops in the fiber; (2) saturating and swelling with water the heat-set fibers thus obtained by treatment with an aqueous bath at a temperature of at least 60° C. and from 1-15° C. and preferably 1-10° C. below the temperature at which damage to the filament such as sticking, occurs in the aqueous medium, for a time sufficient to insure saturation and swelling of the fiber at the temperature employed; (3) drying the swollen fiber in the swollen state whereby

any substantial change in the swollen structure is prevented, and (4) reacting the swollen, substantially water-free heat-set filament, in the presence of an acetalization catalyst, with a monoaldehyde wherein the aldehyde group is directly attached to annular carbon, i. e., a carbon member, of a cyclic structure of at least five atoms and the treatment is continued until at least 25%, but not more than 75%, of the hydroxyl groups in the polyvinyl alcohol have combined with the aldehyde and the resulting fiber has a sticking point above 175° C.

The process of this invention is applicable to oriented fibers of macromolecular, synthetic, linear hydroxylated polymers in which at least 90% (and preferably at least 95%) of the weight consists of vinyl alcohol units, $-\text{CH}_2-\text{CHOH}-$. By "oriented fiber" is meant, as usual, a fiber which has been drawn under tension to an extent such that it shows a typical fiber X-ray diffraction pattern. In general, oriented fibers are obtained when the filament of hydroxylated polymer is stretched at least 300% of its initial length. Filaments of hydroxylated polymer can be drawn in a hot salt bath, e. g., a boiling concentrated solution of sodium dihydrogen phosphate; or they can be drawn in hot oil, or in air at temperatures between 200 and 250° C. Preferably, the filament is drawn to the maximum length short of the breaking point, e. g., with a draw ratio between 3:1 and 11:1, depending on the filament and the drawing conditions. This operation increases the tensile strength of the filament considerably. Various methods of preparing oriented fibers of hydroxylated polymers have been published.

By "macromolecular" is meant a polymer having a degree of polymerization, i. e., a number of recurring units, of at least 100. Suitable polymers include polyvinyl alcohol and hydrolyzed copolymers of vinyl esters with vinylidene, including vinyl, compounds such as ethylene, methyl acrylate, methacrylamide, methyl methacrylate, vinyl thiolacetate, methoxymethoxyethyl methacrylate and the like, comprising at least 90% by weight of polyvinyl alcohol and in which the vinyl ester groups are substantially completely, e. g., at least 99%, hydrolyzed. The preferred polymers for use in this invention are polyvinyl alcohol and the substantially completely hydrolyzed ethylene/vinyl carboxylate polymers (see U. S. 2,386,347) containing between 2 and 10% by weight of ethylene. Any of the standard commercial grades of fiber-forming, substantially completely hydrolyzed polyvinyl alcohol may be used, as well as the highly linear polyvinyl alcohol whose preparation is described in the Cline et al. application Ser. No. 157,634 filed April 22, 1950 as a continuation-in-part of application Ser. No. 19,444, already referred to.

Spinning of the polyvinyl alcohol into filaments may be accomplished by any of the known methods including dry or evaporation spinning. Dry spinning may be carried out by extruding an aqueous solution of the polyvinyl alcohol, e. g., a solution of 25% concentration, into a cell at a temperature of 150–200° C. The yarns so spun are almost free of orientation. They can be drawn to a maximum and relaxed continuously in hot air, or drawn partially or completely and relaxed by a separate baking step. Dry spun yarns have the advantage that they need not be washed exhaustively to remove salts therefrom. Wet spinning into an aqueous salt bath, e. g., a concentrated sodium dihydrogen phosphate bath, (other suitable spinning baths are ammonium

sulfate, ammonium chloride, sodium sulfate, mixtures of disodium hydrogen phosphate and sodium dihydrogen phosphate, etc.) is a preferred method. The fiber may then be oriented by stretching in a hot salt bath, followed by washing and drying at fixed length; or it may be partially stretched in air or in a liquid medium at ordinary temperature, followed by washing, drying at fixed length and finally stretching in air or a nonsolvent liquid medium at 200–240° C. to complete the orientation.

The oriented dry fiber is then subjected to the first step of the process of this invention which is a heating treatment in a substantially anhydrous fluid medium having no solvent action on the fiber, under such conditions that no stretch whatever is imposed on the fiber. Heating the filament under such conditions may be compared to the familiar annealing process. This relaxing or heat-setting is believed to release strains in the filament and induce a higher degree of crystallinity. This heat-relaxing treatment is carried out under tension sufficient to prevent fiber shrinkage of more than 60% but less than that sufficient to stretch the fiber beyond its original length, i. e., under such conditions that the filament may shrink from 0% to 60% of its initial drawn length; in other words, the filament may be permitted no shrinkage (i. e., the heating treatment is done at fixed length, i. e., the original length of the oriented dry fiber), or it may be permitted to shrink to a predetermined value by controlling the conditions of tension. In no case, however, is any stretch applied to the filament. In all cases, the temperature is controlled within a narrow range, between 1° C. and 30° C., and preferably within 2° C. and 20° C., of the temperature at which the filament softens or damage occurs in the heating medium employed, and within the range of 190 to 255° C., and preferably between 210 and 245° C. This may be done by heating the filament at fixed length (e. g., wrapped on a bobbin), when no shrinkage takes place, or by heating the filament in skeins or in the form of staple, when the amount of shrinkage is usually between 25% and 55% of the initial length. Conveniently, the operation is made continuous and the degree of shrinkage is controlled by running the filament through a drawing cell or chamber capable of being heated, with the take-up roll at the same or lower peripheral speed than the feed roll. The relative peripheral speeds of the rolls are adjusted so that either no shrinking takes place or, preferably, between 15% and 30% shrinking is permitted. While the preferred medium for the heat treatment is air or an inert gas such as nitrogen or carbon dioxide, any substantially anhydrous fluid medium which is inert, i. e., does not dissolve or injure the fibers, may be used, including oil, molten paraffin, molten metals or alloys or the like. The treatment is continued until the yarn is in such a condition of crystallinity that it will not shrink more than 10% when subjected to the action of water at 60° C., as this requirement has been found essential to produce a yarn which, after completion of the process, has the properties described below. It will be understood that it is not possible to state accurately the time required for the heat treatment in general, since this time is interdependent with the origin and condition of the fiber, the degree of shrinkage permitted and the temperature used. As a general rule, however, it may be said that, in continuous operation, the heating time

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may be as short as one second and in general a period of three to thirty seconds is sufficient. In batch operations, and particularly when free shrinkage is permitted, the time of treatment may extend from about thirty seconds to forty minutes or even more. In any event, the treatment should be discontinued before the yarn becomes discolored, i. e., takes on an appreciable yellowish or yellow tinge, since when this point is reached the yarn is unsatisfactory for textile fabrics. When the heat treatment is prolonged beyond about ten to fifteen minutes, an inert atmosphere (e. g., nitrogen) should be used in order to prevent the above-mentioned discoloration, presumably due to oxidation, from taking place too soon.

The second step of the process is the activation of the heat-treated fiber by means of a water treatment. It has been found that if this step is omitted the subsequent acetalization reaction is very slow and incomplete and does not lead to resilient fibers. In this step, the fiber (either held at fixed length, e. g., wound up on a bobbin, or, preferably, free to shrink, e. g., as skeins or hanks), is placed in or passed through water or an inert aqueous medium containing at least 50% of water, such as a water-ethanol mixture, at a temperature of at least 60° C. The changes occurring in the yarn by this treatment are not clearly understood but they involve more than mere saturation of the yarn with water since yarn brought to saturation by contact with water at 25° C., even for long periods of time, fails to react in the subsequent acetalization or, if it does, gives a yarn characterized by excessive shrinkage in boiling water. For best results, the bath is maintained at a temperature from 1° C. to about 15° C. below that at which damage to the fiber occurs in the aqueous medium, as shown by sticking of the filaments, or by excessive shrinkage, i. e., shrinkage exceeding about 10% of the length of the heat-treated, relaxed fiber, or by gelation, or by loss of more than 20% of the dry tenacity of the filament. A generally satisfactory temperature range is between 75 and 95° C., although with some especially water resistant fibers, it may be as high as 100° C. or even slightly higher, by operating under pressure. If the fiber is held at fixed length during the activation step it is desirable to use a higher temperature than if it is free to shrink. During the activation treatment the fiber swells, as shown by an increase in its cross-sectional area. The time required for activation of the fiber depends on the size (denier) of the filament, on the bath temperature and on the bath composition, and thus it is not possible to specify definitely a minimum duration. It has been observed, however, that textile size fibers acquire sufficient reactivity in as short a contact time as three seconds at temperatures near the highest permissible. In general, a contact time of ½ to 15 minutes at the preferred temperature range of 75–95° C. is sufficient. The treatment should be interrupted before the fiber has lost 20% of its initial tensile strength, measured dry. Certain water-solvent mixtures permit activation temperatures lower than 60° C.

The third step is the removal or displacement of substantially all the water from the fiber. Again it has been found that if this is omitted the acetalization reaction will not give satisfactory results. Moreover, if too much water is present, the fiber shrinks excessively during the acetalization reaction. Removal of the water should be carried out in such a way that the

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fiber preserves its swollen, activated condition. This can be done by drying the fiber in air at ordinary or slightly elevated temperature, e. g., 50° C.–80° C., and/or at reduced pressure, with or without prior centrifuging, and interrupting the drying as soon as the weight loss shows that substantially all of the water has evaporated. Preferably, it is done by immersing the fiber in a water-miscible organic solvent, preferably a water-miscible alkanol or ether-alkanol of one to six carbons, for a period of five to thirty minutes. It should be noted that if the fourth, or acetalization, step is to be carried out with a large excess, as the solvent, of an aldehyde which is miscible with water (e. g., furfural), the displacement of water from the fiber need not be complete, since the acetalization mixture tolerates more water in such cases.

The last step of the process is the partial acetalization of the fiber with a monoaldehyde of the specific type defined above. Numerous examples of suitable aldehydes will be given as the description proceeds. The acetalization treatment may be carried out in the absence of a solvent if enough of the aldehyde is used to insure good contact with the yarn, but the use of the aldehyde without solvent frequently causes excessive shrinkage during the treatment. The acetalization is preferably carried out in an oxo-free, liquid organic medium which is a solvent for the aldehyde. This medium is preferably a monohydric or dihydric alcohol or ether-alcohol of one to six carbon atoms, e. g., methanol, ethanol, propanol, butanol, hexanol, glycol, diethylene glycol, methoxyethanol, butoxyethanol, etc.; but it may be any other non-oxo solvent such as dibutyl ether, tetrahydrofuran, dioxane, diethylene glycol diethyl ether, and the like. The reaction system should be substantially anhydrous, i. e., it should not contain more than about 5% of water by weight of the total liquid medium. The relative proportions of polyvinyl alcohol and aldehyde are not critical provided there is sufficient aldehyde to react with at least 25% of the hydroxyl groups. The aldehyde is normally used in the proportions of one-fourth to four moles per mole of polyvinyl alcohol, i. e., one-fourth to four moles per hydroxyl equivalent in the polymer and preferably one-half to three moles per mole of polyvinyl alcohol. The "mole" of a polymer such as polyvinyl alcohol is the unit weight of the recurring unit, in this case the $-\text{CH}_2\text{CHOH}-$ unit. The reaction temperature is desirably at least 50° C. and it can be as high as desired short of decomposition of the reactants, a generally useful range being between 70 and 150° C. The reaction is carried out until at least 25%, and preferably at least 30% of the hydroxyl groups in the polyvinyl alcohol have reacted, but it should be stopped before more than about 75% and in most cases before more than about 60% of the hydroxyl groups have reacted. It will be apparent that the required degree of acetalization may vary considerably, depending upon the reactivity and molecular weight of the aldehyde employed. However, it has been found that the limits indicated above will lead to satisfactory products, with the further proviso that, within these limits, the extent of acetalization with any given aldehyde should be controlled so that the sticking point of the final fiber is not below 175° C. Fibers softening below that temperature are unsatisfactory in fabrics which are to be ironed or otherwise subjected to elevated temperatures.

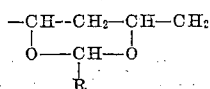
The desired reaction time can easily be deter-

mined by a preliminary test, or by measuring the water evolved when the reaction medium is not miscible with water. Any of the usual acetalization catalysts is suitable, such as phosphoric acid, sulfuric acid, ammonium chloride, sodium bisulfate, calcium chloride, zinc chloride, ferric chloride, oxalic acid, maleic acid, citric acid, boron trifluoride, p-toluenesulfonic acid and the like. In general, the acetalization treatment requires from about ten minutes to twenty hours, depending among other things on the aldehyde used and on the extent of acetalization desired, but under favorable conditions of temperature and concentration it can be carried out in five minutes or even less.

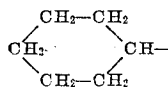
During this treatment, the polyvinyl alcohol fiber shrinks, often considerably, and it gains weight. The most satisfactory products are those in which this weight gain amounts to at least 25% of the original weight.

Optionally, the acetalization step is followed by washing with water and/or weak alkali such as sodium bicarbonate or ammonia to neutralize any acid present, and by a boil-off treatment with water, with or without a detergent. If desired, these two operations may be combined by boiling the yarn with a dilute, e. g., 0.1-1%, solution of sodium hydroxide or sodium carbonate.

The new product of this invention is an oriented polyvinyl alcohol-polyvinyl acetal fiber in which between 25 and 75% of the hydroxyl groups are acetalized by a cyclic aldehyde of the type defined above. The oriented polyvinyl alcohol-polyvinyl acetal fibers consist to the extent of at least 90% of vinyl alcohol, $-\text{CH}_2-\text{CHOH}-$, units and acetalized vinyl alcohol,



units wherein R is a monovalent cyclic radical, preferably of not more than nineteen carbons, with its free valence stemming from a ring of five to six annular atoms, the ratio of acetalized vinyl alcohol units to vinyl alcohol units being between 1:6 and 1:0.66. Thus the R in the acetalized polyvinyl alcohol units in the treated fiber of Examples I, II, V, VIII is



the R in the treated fiber of Example III is C_6H_5- , the R in the treated fiber of Examples IV, XI is $\text{CH}_3-\text{C}_6\text{H}_4-$, the R in the treated fiber of Example VI is the α -furyl radical, the R's in the treated fiber of Examples VII and X are chlorophenyl radicals, the R in the treated fiber of Example IX is a naphthyl radical, etc. Otherwise expressed, the ratio of acetal groups to hydroxyl groups is between 1:6 and 1:0.66. These fibers have a sticking point above 175° C. They are further characterized by the facts that they are insoluble in and substantially unaffected by boiling water, i. e., upon immersion in boiling water for a period of ten minutes the fiber shrinks less than 10% and usually less than 5%, and the loss in dry tensile strength is less than 10% and usually less than 5%. They have a work recovery at 3% elongation (as defined later) of at least 45%, and usually at least 50%. Moreover they have a characteristic internal structure, as shown by X-ray diffraction patterns, which suggests that the fibers are composed of polyvinyl alcohol crystallites in which few, if any, of the hydroxyl groups

are acetalized, and of an amorphous material which is a mixture of polyvinyl alcohol and polyvinyl acetal. It is believed that the chemical structure of the aldehyde used for acetalization together with the particular fiber structure arising from the described method of preparing and processing the fiber are responsible for the high work recoveries of the yarns and the high resilience of the fabrics obtained therefrom.

Work recovery is a measure of the tendency of a yarn to recover from deformation. In general, yarns having high work recovery yield fabrics which have high resilience. Work recovery is defined as the percent of work recovered when a yarn is allowed to recover from a given stretch (or bend, or twist) relative to the work required to accomplish said stretch. It is measured by dividing the area under the stress-strain curve up to a given elongation, obtained when the yarn is allowed to recover, by the area under the curve obtained when the yarn is stretched, and multiplying by one hundred. It has been found that work recovery from elongation of 3% or higher correlates much better with fabric resilience than work recovery from low elongations, e. g., 0.75%.

The invention is illustrated in greater detail in the following examples, in which parts are by weight unless otherwise stated.

EXAMPLE I

Highly linear polyvinyl alcohol was prepared, according to the general procedure described in the Cline et al. application Ser. No. 157,634 filed April 22, 1950 as a continuation-in-part of application Ser. No. 19,444, already referred to, by the following method:

Ten parts of monomeric vinyl acetate mixed with one part of isopropyl alcohol was heated at 50° C. in the presence of 0.5 mole per cent of α, α' -azobis(α, γ -dimethylvaleronitrile) until 31% of the vinyl acetate had polymerized. The polymer was isolated and substantially completely hydrolyzed by treatment with sodium methylate in methanol. The resulting polyvinyl alcohol was made into an aqueous solution containing 18% of polymer, 4% of pyridine and 0.14% of a solubilized long chain phosphate ester. After cooling and deaerating, this solution was extruded through a spinneret into a 45% sodium dihydrogen phosphate aqueous solution at 28° C. After a bath travel of about 60 inches the coagulated yarn was removed from the bath and stretched to a draw ratio of 4.5/1 between positively driven rolls while being passed through a boiling solution of 45-50% sodium dihydrogen phosphate in water. The yarn was then wound up on a bobbin, washed thoroughly in cold water and allowed to dry.

The air-dry oriented yarn was then wound into skeins, dried three to four hours at 105° C. and relaxed by heating in air at 215° C. for two minutes, whereby it shrank about 30% of its initial drawn length. The yarn was then immersed in water at 87° C. for ten minutes. The water was removed from the saturated yarn by centrifuging, immersing in ethanol for 15 minutes and centrifuging again.

Seventy-five parts of the yarn so treated was heated for 15 hours at 82° C. in a solution of 94 parts of hexahydrobenzaldehyde and 890 parts of 92% phosphoric acid in 2600 parts of ethanol. At the end of this treatment the yarn was washed with water, then with 5% aqueous sodium bicarbonate, then with water again and finally it was heated for 30 minutes at 100° C. in a 0.1% aque-

ous solution of technical sodium dodecylsulfate, rinsed and allowed to dry. During the entire treatment the yarn shrank about 39% of its length and gained 36% in weight, which indicated that 34% of the hydroxyl groups had combined with the hexahydrobenzaldehyde.

The treated yarn had a filament denier of 4.0, a tenacity of 1.5 g./d. with 35% elongation, a sticking point of 180° C., a modulus of 23 g./d. and work recoveries of 83% and 48% when elongated 0.75% and 3%, respectively, at 60% relative humidity and at a rate of elongation of 1% per minute. A staple fabric woven from this yarn possessed exceptionally high resilience, comparable to that of high grade wool fabric. When vigorously crumpled by hand, then allowed to relax, the fabric regained its initial shape rapidly and showed substantially no wrinkles or creases.

X-ray diffraction patterns of the above fiber before and after the treatment with hexahydrobenzaldehyde showed that the treated fiber had a higher ratio of amorphous to crystalline material than the untreated one and that the crystalline regions were less oriented. Except for an initial shrinkage of about 6%, the yarn was completely resistant to water at 100° C. and showed no change when immersed in boiling water for long periods of time.

EXAMPLE II

A polyvinyl alcohol/ethylene copolymer containing about 5% of ethylene and obtained by substantially complete hydrolysis of the corresponding polyvinyl acetate/ethylene copolymer was spun by the method described in Example I, except that the yarn was stretched to a draw ratio of 3.7/1 in air instead of in a hot salt solution. After washing and drying, the yarn was finally oriented by a further stretching at a draw ratio of 2.8/1 in air at 215° C. It was then heated in air at 220° C. under controlled tension permitting a shrinkage of 20% of its initial drawn length. The relaxed yarn was made into skeins, heated in water at 85° C. for ten minutes, centrifuged, immersed in ethanol for 15 minutes and centrifuged again. The activated yarn was heated for 15 hours at 75° C. in a solution containing 32 parts of hexahydrobenzaldehyde, 270 parts of 92% phosphoric acid and 698 parts of ethanol. After rinsing, neutralizing and boiling-off in water at 100° C., the yarn had a sticking point of 200° C., a modulus of 30 g./d. and work recoveries of 89% and 51% from elongations of 0.75% and 3%, respectively. The yarn, which had a denier of 91 at the start, shrank 13% during the acetalization treatment exclusive of the boil-off, and it had a denier of 144 just before the boil-off. Calculations based on these figures indicate that the yarn gained about 37% in weight during the treatment, corresponding to acetalization of 35% of the hydroxyl groups in the polymer.

EXAMPLE III

Twenty-seven parts of polyvinyl alcohol yarn spun from the polymer used in Example I and pretreated in exactly the same manner was heated for 60 minutes at 125° C. in a solution containing 155 parts of benzaldehyde, 25 parts of ammonium chloride and 1450 parts of diethylene glycol. The yarn was rinsed, neutralized and boiled-off as described in Example I. The total shrinkage based on the stretch-spun yarn was 37% and the gain in weight was 41%, corresponding to acetalization of 41% of the hydroxyl

groups. The boiled-off yarn had work recoveries of 81% and 57% from elongations of 1% and 3%, respectively, a modulus of 36 g./d. and a tenacity of 2.1 g./d. with 40% elongation, all values being measured at 60% relative humidity and 21° C. The yarn had a sticking temperature of 196° C.

In comparison, an identical yarn was treated with 100 parts of paraformaldehyde along with the same amounts of ammonium chloride and diethylene glycol as above at 125° C. for 90 minutes. The resulting yarn after boil-off had work recoveries of only 47% and less than 20% from elongations of 1% and 3%, respectively. Its sticking temperature was 220° C. In this comparative experiment the over-all shrinkage based on the stretch-spun yarn was 31% and the gain in weight was 8.1%, corresponding to acetalization of 59% of the hydroxyl groups.

EXAMPLE IV

The experiment of Example III was repeated under the same conditions except that 153 parts of p-tolualdehyde was substituted for the benzaldehyde and the acetalization temperature was 115° C. The over-all shrinkage of the yarn during the pretreatment, acetalization and boil-off was 36% based on the stretch spun yarn and the weight gain was 43%, corresponding to acetalization of 37% of the hydroxyl groups. The boiled-off yarn had work recoveries of 74%, 53% and 37% from elongations of 1%, 3% and 5%, respectively. It had a modulus of 32 g./d., a tenacity of 1.9 g./d. and an elongation of 36%. Its sticking temperature was 200° C.

EXAMPLE V

An aqueous solution containing 14.5% of a medium viscosity grade of commercial polyvinyl alcohol was spun as in Example I and the yarn was pretreated as described in that example except that the hot water treatment was carried out at 85° C. The yarn was then heated for 16 hours at 75° C. in a solution containing 28 parts of hexahydrobenzaldehyde, 200 parts of 92% phosphoric acid and 772 parts of ethanol. Following washing and drying, the over-all shrinkage, based on the stretch spun yarn, was 50%. When the yarn was boiled in a 0.1% aqueous solution of technical sodium dodecyl sulfate for one hour, it shrank 6%. The boiled-off yarn had gained 47% in weight, corresponding to acetalization of 43% of the hydroxyl groups. It had work recoveries of 76% and 49% from elongations of 1% and 3%, respectively, a tenacity of 1.4 g./d., a sticking temperature of 181° C., and a modulus of 12 g./d.

Similar results were obtained when the same type yarn was relaxed by heating in skeins in air at 200° C. for 20 minutes whereupon it shrank 30.5%, when treated for 10 minutes in water at 80° C., squeezed, soaked in ethanol for 15 minutes and subjected to a similar treatment with hexahydrobenzaldehyde. At the end of the treatment the yarn had gained 40% in weight, and it had work recoveries of 69% and 47%, respectively, from 1% and 3% elongations. When the heat-relaxing treatment was carried out for 40 minutes at 200° C. the yarn gained 32% in weight on subsequent acetalization with hexahydrobenzaldehyde as above.

A similar yarn, dried at 105° C. for 2½ hours, was relaxed in air at 215° C. for two minutes in skein form, whereupon it shrank 51%, then activated in water at 85° C. for 10 minutes and subjected to a similar treatment with hexahydro-

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benzaldehyde. The yarn showed a weight gain of 44%, work recoveries of 73% and 51% from elongations of 1% and 3%, respectively, a tenacity of 1.3 g./d. with 57% elongation and a modulus of 14 g./d.

EXAMPLE VI

A commercial grade of medium viscosity polyvinyl alcohol was spun into fibers as in Example I except that the solution concentration was 13.5% and no pyridine was used. The filament was further treated as in Example I except that the water-activation treatment was carried out at 85° C. Three parts of the yarn was heated for 40 minutes at 112° C. in a bath composed of 150 parts of furfural and one part of citric acid. After washing and drying, the over-all shrinkage based on the stretch spun yarn was 53%. When the yarn was boiled in a 0.1% aqueous solution of technical sodium dodecylsulfate for one hour, it shrank 6%. The boiled-off yarn had gained 41% in weight, corresponding to acetalization of 46% of the hydroxyl groups. It had work recoveries of 71% and 51% from elongations of 1% and 3%, respectively; a tenacity of 1.4 g./d. at 59% elongation, a modulus of 19 g./d. and a sticking point above 220° C.

EXAMPLE VII

A polyvinyl alcohol yarn similar to that used in Example VI was activated for ten minutes in water at 86° C. The water was displaced from the yarn by successive immersion in alcohol and diethylene glycol, then the yarn was heated for 40 minutes at 125° C. in a bath composed of 40 parts of o-chloro-benzaldehyde, three parts of 92% phosphoric acid and 230 parts of diethylene glycol. After washing and drying, the over-all shrinkage based on the stretch spun yarn was 47%. When the yarn was boiled in a 0.1% aqueous solution of sodium dodecylsulfate for one hour it shrank 2%. The boiled-off yarn had gained 58% in weight, corresponding to 42% acetalization of the hydroxyl groups. It had work recoveries of 70% and 48% from elongations of 1% and 3%, respectively, a tenacity of 1.1 g./d. at 38% elongation, a modulus of 17 g./d. and a sticking point of 212° C.

EXAMPLE VIII

A copolymer containing 91.3% vinyl alcohol, 4.5% methyl methacrylate and 4.1% methacrylamide was made into an aqueous solution containing 17.3% of the polymer, 0.2% of sodium hydroxide and 0.14% of a long chain solubilized phosphate ester. The solution was spun and the yarn was stretched, washed and dried as in Example I. The yarn in skein form was dried further at 105° C. and heat-treated in air at 220° C. for one minute, whereupon it shrank about 41%. The skein was then immersed in water at 80° C. for ten minutes, squeezed, immersed in ethanol for 15 minutes, squeezed and treated for 15 hours at 75° C. in a solution containing 23 parts of hexahydrobenzaldehyde, 354 parts of 92% phosphoric acid and 1030 parts of ethanol. Following neutralization, washing and boil-off the yarn was found to have work recoveries of 84% and 54% from elongations of 0.75% and 3%, respectively. Its tenacity was 1.9 g./d. with an elongation of 46% and its modulus was 26 g./d.

EXAMPLE IX

A polyvinyl alcohol yarn prepared as in Example VI was heated in skein form in air at 215° C. 75

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for two minutes, during which it shrank 41%, and activated in water at 86° C. for ten minutes. After displacing the water by immersion in ethanol, then in diethylene glycol, the yarn was treated in a bath composed of 12 parts of alpha-naphthaldehyde, 2 parts of 92% phosphoric acid and 71 parts of diethylene glycol for 45 minutes at 115° C. Following this treatment the yarn was washed successively in ethanol, dilute aqueous sodium bicarbonate and water, and boiled one hour in water, during which time it shrank 3% in length. The weight gain of the yarn was 52%. It had work recoveries of 72% and 49% from 1% and 3% elongations, respectively, a sticking point of 218° C. and a dry tenacity of 1.9 g./d. with 35% elongation.

EXAMPLE X

A polyvinyl alcohol yarn was prepared, heat relaxed and water-activated as in Example IX. The shrinkage was 35%. After displacing the water by immersion in ethanol, then in diethylene glycol, the yarn was heated for 60 minutes at 125° C. in a bath consisting of 21 parts of 2,6-dichlorobenzaldehyde, four parts of 92% phosphoric acid and 94 parts of diethylene glycol. The treated yarn was washed successively with ethanol, sodium bicarbonate and water and boiled in water for one hour, during which it shrank 2%. The weight gain was 57%. The yarn had work recoveries of 68% and 48% from elongations of 1% and 3%, respectively, a sticking temperature of 204° C. and a dry tenacity of 1.4 g./d. with 46% elongation.

EXAMPLE XI

An oriented polyvinyl alcohol yarn was wound on a bobbin. The yarn, thus held at constant length, was heated for five minutes in oil at 225° C., then extracted with benzene to remove excess oil. It was then wound into a skein, activated by immersion in water at 85° C. for ten minutes, and soaked in alcohol to remove excess water. The swollen, dried yarn was treated for 60 minutes at 113° C. in a solution consisting of 11.3 parts of p-tolualdehyde, one part of 92% phosphoric acid and 82 parts of diethylene glycol. The yarn was neutralized, rinsed and boiled-off as in the preceding examples. It was found to have gained 41% in weight. The yarn shrank 20% during activation and acetalization and an additional 5% during the boil-off. It had work recoveries of 68% and 45% from elongation of 1% and 3%, respectively, and a dry tenacity of 2.0 g./d. with 36% elongation.

In addition to the aldehydes shown in the examples, there may be used in the process of this invention any monoaldehyde having at least one ring of at least five members with the aldehyde group attached directly to an annular carbon thereof. Further examples are p-ethylbenzaldehyde, 2,4-dimethylbenzaldehyde, 5-methylfurfural, p-benzylbenzaldehyde, thiophenealdehyde, m-nitrobenzaldehyde, beta-naphthaldehyde, and the like.

The above-described structural requirements are based on observations which indicate that, in order to produce the new and improved fibers of this invention, it is necessary that the aldehyde group be as close as possible to the cyclic structure. This is illustrated by the fact that phenylacetaldehyde or hydrocinnamaldehyde do not produce fibers having outstanding work recoveries. The presence of a ring structure is essential, as shown by the fact that acyclic alde-

hydes such as chloroacetaldehyde, butyraldehyde, crotonaldehyde, 3,5,5-trimethylhexanal and 2-n-propyl-2-heptenal, when used in the process of this invention, give yarns having low work recoveries and usually also low resistance to boiling water. Formaldehyde gives poor resilience, i. e., inferior work recovery from 3% elongation. Aldehydes of 5 to 11 carbons having the aldehyde, —CHO, group attached to nuclear carbon of a ring of 5 to 6 annular atoms give excellent results as exemplified in the above examples. Aldehydes of five to seven carbons, containing only carbon, hydrogen, and oxygen and with the —CHO group as the only substituent on the nucleus, are preferred.

For purposes of comparison, the following table shows the work recoveries from 3% elongation and the block sticking temperatures which were observed with oriented polyvinyl alcohol yarns treated, according to the process of this invention, with (a) the aldehydes of the examples; (b) other monoaldehydes having at least one ring of at least five members with the aldehyde group attached directly to an annular carbon thereof; and (c) aldehydes which are either aliphatic or aromatic but, in the latter case, do not correspond to the above definition. In each case the amount of acetalization is given. The difference between operable and inoperable aldehydes, as regards work recovery and, in some cases, sticking point is apparent at a glance.

Properties of acetalized polyvinyl alcohol yarns

Aldehyde Used	Percent Molar Substitution	Percent Work Recovery, 3 Percent Stretch	Block Stick, Temp., ° C.
Hexahydrobenzaldehyde	34	48	180
Benzaldehyde	41	57	196
p-Tolualdehyde	37	53	200
Furfural	46	51	>220
o-Chlorobenzaldehyde	42	48	212
α-Naphthaldehyde	33	49	218
2,6-Dichlorobenzaldehyde	32	48	204
4-Phenylbenzaldehyde	31	46	198
9-Anthraldehyde	43	51	230
p-Chlorobenzaldehyde	35	55	206
2,4-Dichlorobenzaldehyde	37	54	206
3,4-Dichlorobenzaldehyde	46	51	196
Formaldehyde	59	<20	220
Crotonaldehyde	58	19	110
2-n-Propyl-2-heptenal	8	14	200
3,5,5-Trimethylhexanal	31	25	182
n-Butyraldehyde	42	26	155
2-Methylbutyraldehyde	39	32	140
Isovaleraldehyde	41	31	180
n-Heptaldehyde	30	24	175
β-Phenylpropionaldehyde	42	27	145
Phenylacetaldehyde	68	33	190

Of the aldehydes defined above, the preferred ones are those which contain up to twenty carbon atoms, for the reason that materials of higher molecular weight tend to give yarns of increased plasticity and increased sensitiveness to organic solvents. Still more preferred are the aldehydes of five to twenty carbon atoms in which any atoms which may be present in addition to carbon, hydrogen and the carbonyl oxygen, are halogen, particularly chlorine, and cyclic oxygen, i. e., oxygen which is part of a ring structure. Particularly good results have been obtained with benzaldehyde, hexahydrobenzaldehyde and furfural.

It should be understood that aldehydes within the defined class may vary rather widely in activity. Certain aldehydes may be relatively unreactive, for example because of steric hindrance caused by multiple or heavy substitution on the carbons adjacent or near to the carbonyl group. Due allowance must be made for such

variations in reactivity, which are apparent to the skilled chemist.

The yarns obtained in accordance with this invention are particularly useful in the manufacture of fabrics for wearing apparel, curtains, drapes, blankets, etc., in view of their great resilience and of their insensitivity toward boiling water and dry cleaning solvents. They are also useful in many other applications such as the manufacture of filter cloths, awnings, tents, wrapping material, etc.

The term "dry" is used as in Webster-Merriam—New International Dictionary—to denote "free from water."

The foregoing detailed description has been given for clearness of understanding only and no unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described for obvious modifications will occur to those skilled in the art.

What is claimed is:

1. A method of improving oriented filaments of linear synthetic polymers in which from 45 to 50% of the carbon atoms of the linear polymer chain are attached to hydroxyl groups which polymers consist to the extent of at least 90%, by weight, of vinyl alcohol, —CH₂CHOH—, units, any remainder being polymerizable vinylidene compound units, which comprises heating the oriented filaments under tension controlled to prevent more than 60% shrinkage referred to the initial drawn length of the fiber at a temperature within the range of 190–255° C. and within the range from 1° C. below to 30° C. below the softening point of the filaments for a time between about one second and about forty minutes until the filaments shrink not more than 10% when immersed in water at 60° C. and dried, the heating at 190–255° C. being discontinued before the filaments become discolored; swelling the filaments by immersion in an inert aqueous medium containing 50–100% water at a temperature of at least 60° C. but not higher than 1° C. below the temperature at which the filaments stick together for a time between about three seconds and about fifteen minutes until the filaments are saturated but discontinuing the immersion before the filaments have lost 20% of their initial dry tensile strength; drying the filaments in their swollen condition; and treating the substantially water-free, swollen, heat-set, oriented filaments in an inert, substantially anhydrous medium with a monoaldehyde of up to twenty carbons having the aldehyde, —CHO, group attached to annular carbon of a cyclic nucleus of at least five annular atoms at a temperature of at least 50° C. but below the decomposition point of the reactants until, as indicated by gain in weight, 25–75% of the hydroxyl groups in the filament have reacted with the aldehyde.

2. Process of claim 1 wherein the oriented filaments essentially consist of vinyl alcohol,



units.

3. Process of claim 1 wherein the aldehyde has 5 to 11 carbons and has the aldehyde group attached to annular carbon of a ring of 5 to 6 annular atoms.

4. Process of claim 3 wherein the oriented filaments essentially consist of vinyl alcohol,



units.

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5. Process of claim 1 wherein the aldehyde is benzaldehyde.

6. Process of claim 1 wherein the aldehyde is hexahydrobenzaldehyde.

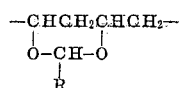
7. Process of claim 1 wherein the aldehyde is a toluanaldehyde.

8. Process of claim 1 wherein the aldehyde is a chlorobenzaldehyde.

9. Process of claim 1 wherein the aldehyde is a naphthaldehyde.

10. Process of claim 1 wherein the aldehyde is an aldehyde of 5-11 carbons, contains only carbon, hydrogen, and oxygen, and the $-\text{CHO}$ group is the only substituent on the nucleus.

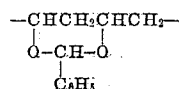
11. An oriented synthetic linear polymeric filament consisting to the extent of at least 90% of vinyl alcohol, $-\text{CH}_2\text{CHOH}-$, units and acetalized vinyl alcohol,



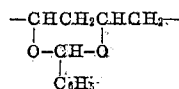
units wherein R is a monovalent cyclic radical of up to nineteen carbons with its free valence stemming from annular carbon of a nucleus of at least five annular atoms, any remainder being polymerizable vinylidene compound units, the ratio of acetalized vinyl alcohol units to vinyl alcohol units being between 1:6 and 1:0.66, said filament having a work recovery at 3% elongation of at least 45%.

12. The oriented filament of claim 11 wherein the polymer consists essentially of the vinyl alcohol units and acetalized vinyl alcohol units of claim 11.

13. An oriented synthetic linear polymeric filament consisting to the extent of at least 90% of vinyl alcohol, $-\text{CH}_2\text{CHOH}-$, units and units of the formula.

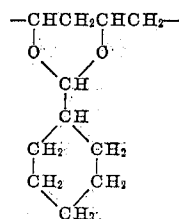


any remainder being polymerizable vinylidene compound units, the ratio of units of the formula



to the vinyl alcohol units being between 1:6 and 1:0.66, said filament being insoluble in boiling water, substantially unaffected in dry tensile strength and shrinkage therein, of sticking point of at least 175° C., and of work recovery at 3% elongation of at least 45%.

14. An oriented synthetic linear polymeric filament consisting to the extent of at least 90% of vinyl alcohol, $-\text{CH}_2\text{CHOH}-$, units and units of the formula:

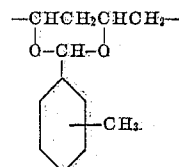


the ratio of said latter units to the vinyl alcohol units being between 1:6 and 1:0.66, said filament

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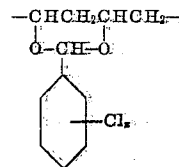
being insoluble in boiling water, substantially unaffected in dry tensile strength and shrinkage therein, of sticking point of at least 175° C., and of work recovery at 3% elongation of at least 45%.

15. An oriented synthetic linear polymeric filament consisting to the extent of at least 90% of vinyl alcohol, $-\text{CH}_2\text{CHOH}-$, units and units of the formula:



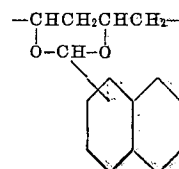
the ratio of said latter units to the vinyl alcohol units being between 1:6 and 1:0.66, said filament being insoluble in boiling water, substantially unaffected in dry tensile strength and shrinkage therein, of sticking point of at least 175° C., and of work recovery at 3% elongation of at least 45%.

16. An oriented synthetic linear polymeric filament consisting to the extent of at least 90% of vinyl alcohol, $-\text{CH}_2\text{CHOH}-$, units and units of the formula



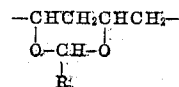
wherein x is an integer from 1 to 2, the ratio of said latter units to the vinyl alcohol units being between 1:6 and 1:0.66, said filament being insoluble in boiling water, substantially unaffected in dry tensile strength and shrinkage therein, of sticking point of at least 175° C., and of work recovery at 3% elongation of at least 45%.

17. An oriented synthetic linear polymeric filament consisting to the extent of at least 90% of vinyl alcohol, $-\text{CH}_2\text{CHOH}-$, units and units of the formula



the ratio of said latter units to the vinyl alcohol units being between 1:6 and 1:0.66, said filament being insoluble in boiling water, substantially unaffected in dry tensile strength and shrinkage therein, of sticking point of at least 175° C., and of work recovery at 3% elongation of at least 45%.

18. An oriented synthetic linear polymeric filament consisting to the extent of at least 90% of vinyl alcohol, $-\text{CH}_2\text{CHOH}-$, units and acetalized vinyl alcohol,



units wherein R is the monovalent radical R of an aldehyde RCHO of 5-11 carbon atoms containing only carbon, hydrogen and oxygen wherein the $-\text{CHO}$ group is joined to annular carbon and is the only substituent on a nucleus of at least five annular atoms, the ratio of acetalized vinyl alcohol units to vinyl alcohol units being between 1:6 and 1:0.66 and any polymer units

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other than polyvinyl alcohol units and acetalized polyvinyl alcohol units being polymerizable vinylidene compound units, said filament being insoluble in boiling water, substantially unaffected in dry tensile strength and shrinkage therein, of sticking point of at least 175° C., and of work recovery at 3% elongation of at least 45%.

19. The oriented filament of claim 18 wherein the polymer consists essentially of the vinyl alcohol units and acetalized vinyl alcohol units of claim 18.

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