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SHAPED ARTICLES OF POLYVINYL ALCOHOL POLYMER BLENDS

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This invention relates to improved synthetic fibers of polyvinyl alcohol. More specifically, the invention relates to polyvinyl alcohol fibers having improved dyeability for direct colours, acid colors, and acid mordant colors, and also having high resistance to boiling water, and to a process for manufacturing such fibers.

It is well known that fibers of hydroxylated polymers such as polyvinyl alcohol or hydrolyzed copolymers of vinyl esters with minor amounts of polymerizable vinyl or vinylidene compounds can be obtained by dry or wet spinning from aqueous solutions thereof. However, such fibers show undesirable sensitivity to water, especially hot water. The fibers generally shrink more than 10% of their length in water at room temperatures, and dissolve in hot water at 70–90° C.

In order to improve the properties of the fibers, the spun fibers are usually subjected to a heat treatment at temperatures in the range of 200–250° C. followed by acetalization with formaldehyde. By heat treatment the wet softening temperature of the fibers, that is the temperature at which the fibers shrink 10% of their length when immersed for 30 minutes in water, can be raised to 60–100° C., while the fibers still dissolve in water of 70–110° C. If after heat treatment the fibers are further reacted with formaldehyde, the wet softening temperature can be raised to 100–130° C. and the fibers do not dissolve in 150° C. water. Fibers so treated have sufficient wet heat resistance for practical uses.

A disadvantage of polyvinyl alcohol fibers treated as above indicated is that these fibers have poor dyeability. Since polyvinyl alcohol fibers do not contain basic nitrogen, they are not readily dyed with acid colors or with acid mordant colors. Untreated polyvinyl alcohol fibers may have dyeability similar to cellulose fibers with direct colors due to the presence of hydroxyl groups, but heat treatment adversely affects dyeability with direct colors such that after heat treatment the dyeability is almost the same or poorer than that of cotton fibers. By acetalization after heat treatment, the dyeability with direct colors usually decreases further as a result of the reaction of accessible hydroxyl groups. Dye absorption of heat treated and acetalized polyvinyl alcohol fibers with respect to direct colors is usually about 30–80% that of cotton.

Polyvinyl alcohol fibers which are acetalized in aqueous solution directly after being spun without intermediate heat treatment, have good affinity for direct dyes. That is believed due to the increase in accessible hydroxyl groups resulting from swelling of the fibers during acetalization, which increase more than offsets blocking of hydroxyl groups as a result of acetalization. However, the wet softening temperature of the fibers is usually below about 60° C. and the fibers shrink considerably in boiling water and become gelatinous and sticky. If the degree of acetalization is increased, the affinity for direct dyes decreases greatly while the resistance to shrinkage in boiling water is still poor.

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It is an object of this invention to provide polyvinyl alcohol fibers having improved dyeability.

It is a further object of this invention to provide polyvinyl alcohol fibers having good dyeability and high wet heat resistance.

Still another object of the invention is to provide a method for producing such improved polyvinyl alcohol fibers.

Other objects of the invention will be apparent from the following specification and claims.

In accordance with the present invention, a homogeneous, single phase aqueous spinning solution is prepared for the production of polyvinyl alcohol fiber, which solution contains polyvinyl alcohol and a water soluble polymer resulting from the polymerization of a nitrogen-containing compound, said polymer being effective to impart improved dyeability to the fibers prepared from the spinning solution. Proportions of the spinning solution components are regulated such that the percentage of nitrogen based on the weight of all the polymers contained therein is in the range of 0.1–5%. Polymer concentration in the spinning solution is usually about 10–25% for wet spinning processes used, about 25–50% for dry spinning processes.

The spinning solution is then extruded into a medium effective to remove water therefrom and to form filaments, said medium usually being air or an inert gas such as nitrogen at temperatures of 50–180° C. in dry spinning techniques or being a concentrated aqueous coagulating solution of a salt such as sodium sulfate or ammonium sulfate at temperatures of 25–60° C. in wet spinning processes.

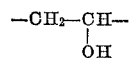
Filaments obtained by the above spinning processes are stretched to a draw ratio of 2:1–12:1. For wet spun filaments, the stretching can be carried out directly after spinning while the fibers are wet at room temperature up to 100° C. to a draw ratio of about 5:1. For stretching to higher draw ratios, it is preferred to conduct the stretching in a heated medium such as air at 100–250° C.

The oriented filaments are then subjected to heat treatment until the filaments have a wet softening temperature of higher than 60° C. This is attained usually by heating the filaments in a medium such as air at 210–250° C. for 2 seconds to 5 minutes.

The heat set and oriented filaments are then acetalized by reaction with an aldehyde having up to about 20 carbon atoms until about 5–50% of the polyvinyl alcohol hydroxyl groups have been acetalized. The acetalization is conveniently carried out in an aqueous solution containing 0.2–10% aldehyde, 5–20% sulfuric acid, and 0–25% sodium sulfate or ammonium sulfate at temperatures of 40–80° C. for times ranging from a few minutes, e.g. 10 minutes to several hours, e.g. 5 hours.

The polyvinyl alcohol fibers prepared in accordance with the present invention have greatly improved dyeability with acid colors, acid mordant colors, and direct colors and also have high wet heat resistance and good mechanical properties.

The polyvinyl alcohol employed in carrying out the invention is a linear synthetic polymer consisting of at least 98% vinyl alcohol units

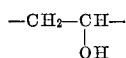


Polyvinyl alcohol having a degree of polymerization greater than 800 and preferably in the range 1,000–3,000 is employed.

As described above, a water soluble polymer resulting from the polymerization of a nitrogen-containing compound, which polymer is effective to improve fiber dyeability is dissolved in the spinning solution together with the polyvinyl alcohol to form a single phase, homo-

geneous spinning solution. Molecules of said nitrogen-containing polymer are subsequently uniformly distributed throughout the fiber. In order to obtain good dyeing properties, the amount of nitrogen in the spinning solution is regulated between 0.1 and 5% by weight of the total weight of polymers. Below 0.1% nitrogen, inadequate improvement in dyeability is obtained while 5% by weight nitrogen represents a practical upper limit above which there is no significant gain in dyeability.

In order to insure preparation of fibers having high water resistance and good mechanical properties characteristic of polyvinyl alcohol fibers, polyvinyl alcohol consisting of at least 98% vinyl alcohol units



should comprise at least 30% by weight of the polymers in the spinning solution.

The water soluble polymers prepared by polymerization of a nitrogen-containing compound which are effective to improve the dyeing properties of polyvinyl alcohol fibers include polymers prepared by free radical or ionic polymerization as well as polymers prepared by condensation polymerization. The polymerization is so conducted that the nitrogen compound comprises at least 0.2 mol percent of the final polymer. Especially preferred water soluble polymers prepared by polymerizing nitrogen compounds are polymeric amino alcohols and derivatives thereof, polymeric alkylenimines, polymeric amines, polyaminotriazoles, polymeric amides, and copolymers of vinyl alcohol and nitrogen containing monomers.

By polymeric aminoalcohols as used herein is meant the water soluble products resulting from the condensation of ammonia, a primary amine or a di-secondary amine with epihalohydrins, dihalohydrins or diepoxides.

Illustrative of suitable primary amine and di-secondary amine reactants are methyl amine, ethyl amine, propyl amines, butyl amines, cyclohexyl amine, N,N'-dimethyl ethylene diamine, N,N'-dimethyl proxylenediamine, N,N'-dimethyl hexamethylene diamine, piperazine, and the like.

Epichlorohydrin, epibromohydrin, 2,3-epoxy-4-chlorobutane, 1,2-epoxy-4-chlorobutane, 1,2-dichloro-3-hydroxy propane, 1,3-diamino-2-hydroxy propane, butadiene diepoxide, chlorobutadiene diepoxide, isoprene diepoxide, vinyl cyclohexene diepoxide and the like are illustrative of the epihalohydrin, dihalohydrin, or diepoxide reactants.

The condensation polymerization is carried out in accordance with known techniques. Usually an excess of the basic material is employed. Molecular weights of the water soluble polymeric aminoalcohols are above about 200, usually in the range 200-1500. Derivatives of the polymeric amino alcohols can be employed including derivatives prepared by reacting the polymeric aminoalcohols with chloroacetic acid or chloroacetaldehyde dimethyl acetal.

Water soluble polymeric alkylenimines, especially polymeric ethylenimine, are useful in accordance with the invention to impart improved dyeability to the polyvinyl alcohol fibers. These polymers are prepared by known methods.

Water soluble polymeric amines such as polyvinyl amine, polyvinyl pyridine, poly(2-methyl-5-vinyl pyridine), poly(2-vinyl-5-ethyl pyridine), and the like are suitably employed in the invention. Salts of the polymeric amines formed by neutralizing the polymeric amines with a strong acid such as hydrochloric acid, sulfuric acid, trifluoroacetic acid, trichloroacetic acid, and the like are very useful in practise of the invention.

Copolymers of the amines with other monomers, which copolymers are water soluble, can be employed in the invention. Amines such as vinyl pyridine and the like can be copolymerized with comonomers such as vinyl acetate by known methods to form water soluble polymers useful in the invention. Alternatively, such copoly-

mers can be saponified to produce water soluble vinyl amine-vinyl alcohol copolymers which also are useful in accordance with the invention to improve dyeability of polyvinyl alcohol fibers. Other comonomers include methyl acrylate, acryl amide, and the like. The water soluble polymeric amines and copolymers thereof are prepared by known polymerization methods. Polymeric amines having molecular weight above about 500 are desirable for use in the invention. In the case of copolymers, it is important that the nitrogen-containing monomer comprise at least 0.2 mol percent of the resulting polymer.

Water soluble polyaminotriazoles are useful in accordance with the invention for improving the dyeing properties of polyvinyl alcohol fibers. These polyaminotriazoles are prepared by known methods, for example, by heating succinic acid with hydrazine hydrate together with small amounts of acetamide.

Water soluble polymeric amides are very useful in the practise of the invention. Water soluble polyvinyl pyrrolidones including polyvinyl pyrrolidone and polymeric derivatives such as poly(1-vinyl-5-methyl-2-pyrrolidone), poly(1-vinyl-4-ethyl-2-pyrrolidone), poly(1-vinyl-5-ethyl-2-pyrrolidone) as well as poly(N-vinyl caprolactam), poly(N-vinyl valerolactam) and the like greatly improve the dyeability of polyvinyl alcohol fibers.

Water soluble copolymers of the polymeric amides can be used. Water soluble copolymers with vinyl acetate, vinyl propionate, or other vinyl esters of organic acids are suitable in the invention. Partially or completely saponified derivatives of these copolymers may be used.

Additionally, water soluble copolymers of the polymeric amides with acrylamide, acrylonitrile, acrylic acid, methyl acrylate, methacrylamide, maleic anhydride, styrene, vinyl chloride, vinyl methyl ketone, vinyl methyl ether, N-vinyl succinic amide, N-vinyl phthalimide and the like can be employed in practice of the invention. Usually the amide comprises at least 30-50 mol percent of the copolymer to insure sufficient copolymer water solubility.

Water soluble copolymers of vinyl alcohol and a nitrogen-containing monomer containing at least 0.2 mol percent of the nitrogen-containing monomer are useful in the invention. These copolymers can be prepared by saponification of the copolymer of a vinyl ester such as vinyl acetate or the like with a nitrogen-containing monomer.

Examples of nitrogen-containing monomers which can be copolymerized with vinyl esters such as vinyl acetate by known means to produce copolymers which are saponified and used in the invention are 2-vinyl pyridine, 4-vinyl pyridine, vinyl pyrazine, 2-methyl-5-vinyl pyridine, N-vinyl imidasol, vinyl quinoline, vinyl thiazol, N-vinyl pyrrolidone, allyl amine, N,N-diethyl allyl amine, vinyl phthalimide, and the like.

Copolymers of vinyl alcohol and nitrogen-containing monomers can be made by alternative methods such as by copolymerizing a halogen-containing monomer such as allyl chloride or a carboxyl containing monomer such as methyl vinyl ketone with a vinyl ester and subsequently reacting the polymer with ammonia or an amine. Such copolymers are included within the scope of the present invention.

Illustrative of the aldehydes which can be used in insolubilizing the fibers of the present invention are formaldehyde, chloroacetaldehyde, butyraldehyde, benzaldehyde, glyoxal, terephthalic aldehyde, and the like. Other insolubilizing methods such as reaction with titanium sulfate or a chromate can also be employed.

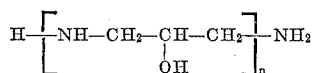
While the invention is primarily directed to the production of improved fibers, it will be understood that other shaped articles such as bristles, tubes, rods, fibers and the like having improved dyeability can also be prepared by the invention.

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Example I

Epichlorohydrin in amount of 90 grams was added to a large excess of aqueous ammonia solution containing 28% by weight ammonia. The resulting mixture underwent exothermic reaction. After the reaction had subsided, the mixture was evaporated to about one half the original volume to complete the reaction.

Water was added to bring the volume of the mixture to its original level. HCl was removed from the solution by contact with a strongly basic anion exchange resin. The solution was then evaporated to a polymer concentration of about 50% by weight. Nitrogen content of the solution was about 9.82% by weight. The amino-alcohol polymer was a water soluble material having the general formula



and having a molecular weight in the range of 200-1500, the subscript n in the foregoing formula and in the formulae of Examples VI and VII designating the number of the bracketed units in the polymer molecule and varying in magnitude in dependence upon the degree of polymerization.

This solution was added to a 15% by weight aqueous solution of polyvinyl alcohol in amount of about 3% of the polyvinyl alcohol solution.

The resulting homogeneous, single phase solution was wet spun by extrusion into an aqueous substantially saturated solution of sodium sulfate. After drying, the nitrogen content of the resulting fiber was about 1.2% by weight.

The fiber was drawn 5 seconds at 235° C. to 2.8 times its length and then heat treated at constant length for 10 seconds at 240° C.

Subsequently the fiber was acetalized in an aqueous solution of 12% sulfuric acid, 15% sodium sulfate and 5% formaldehyde for 1 hour at 70° C. Degree of acetalization was 34%. The fiber thus obtained underwent only slight shrinkage in boiling water. The fiber had a softening point in air of 228° C. Dry tenacity of the fiber was 6.68 grams per denier and dry elongation was 21%.

The dye absorption of the fiber was tested by dyeing in a bath containing Nippon Fast Violet (Colour Index No. 27905) in amount of 2% by weight of fiber, a direct dye, and Acid Brilliant Scarlet 3R (Colour Index No. 16255), 4% by weight of fiber, an acid dye. Dye bath exhaustion was measured after 1 hour at 80° C. The direct dye was 100% exhausted and the acid dye was 68% exhausted.

By way of comparison polyvinyl alcohol, alone, when similarly spun, hot drawn, heat treated and acetalized to 28% degree of acetalization, gave a fiber which did not shrink substantially in boiling water and which had a softening point in air of 224° C. The fiber had a dry tenacity of 7.3 grams per denier, and dry elongation of 19.4%. However, direct dye exhaustion was only 7.5% while acid dye absorption was 0%.

Example II

Epichlorohydrin and aqueous ammonia were reacted as described in Example I. After treatment with anion exchange resin to remove HCl, the polymer solution was evaporated until a white wax-like polymeric amino-alcohol was obtained.

This polymer was dissolved in amount of 1% by weight to an aqueous 15% by weight solution of polyvinyl alcohol. The resulting solution was wet spun as described in Example I. After drying the resultant fiber had a nitrogen content of about 0.7% by weight. The fiber was drawn to 2.9 times its length in 5 seconds at 235° C. and heat treated at 240° C. for 10 seconds at constant length.

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The fiber was acetalized in aqueous solution containing 10% sulfuric acid, 15% sodium sulfate, and 5% formaldehyde for 1 hour at 70° C. Degree of acetalization was 31%. The fiber thus obtained underwent very little shrinkage in boiling water.

The fiber dyeability was tested by dyeing in a bath containing a direct dye Direct Green BC (Colour Index No. 30290), 2% by weight of fiber, and in a bath containing an acid dye, Acid Brilliant Scarlet 3R (Colour Index No. 16255), 4% by weight of fiber, at 60° C. for 1 hour. Dye bath exhaustion was about 100% in each case. The fiber did not shrink during dyeing.

By way of comparison, when just polyvinyl alcohol was spun and after treated as above described, direct dye exhaustion was 13% and acid dye exhaustion was 0%.

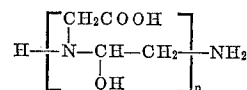
Example III

Epichlorohydrin and aqueous ammonia were reacted as described in Example I. After treatment with anion exchange resin to remove HCl the resulting polymer solution was divided into two parts, parts A and B.

Part A was admixed with aqueous solution containing about 13% chloroacetic acid and about 20% sodium carbonate.

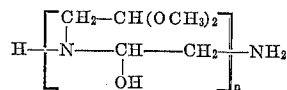
Part B was admixed with a solution of chloroacetaldehyde dimethyl acetal in ethyl alcohol.

Both solutions were heated and after completion of the reactions were dialyzed in running water. Yellow amorphous water soluble polymers were obtained. The polymer from part A had the probable formula



and had a nitrogen content of about 14% by weight.

The polymer from part B had the probable formula



and had a nitrogen content of about 15% by weight.

The polymers from part A and B were respectively dissolved in different aqueous solutions of 15% by weight polyvinyl alcohol in amounts of 1.9% and 1.6% by weight of the solutions.

The solutions were wet spun as described in Example I. After orienting the resulting fibers, the fibers were heat treated at constant length for 10 seconds at 230° C. The fibers were then acetalized in aqueous solutions containing 10% sulfuric acid and 5% formaldehyde at 70° C. for 1 hour. Each fiber was acetalized to a degree of acetalization of 31%.

The fibers were tested for dye absorption in the same manner as described in Example I. Direct dye bath exhaustion was 100% for each. Acid dye bath exhaustion was 60-70% for each fiber.

Example IV

Epibromohydrin in amount of 200 grams was added to 500 grams of 30% by weight aqueous solution of ammonia. The reaction was carried out as described in Example I. HBr was removed by contact with strongly basic anion exchange resin and the resulting polymer solution was concentrated to about 50% by weight of water soluble polymeric amino-alcohol having the same formula as the polymer obtained in Example I. The molecular weight of the polymer was in the range 200-1500. The polymer solution had a nitrogen content of 10.11% by weight.

The polymer solution was added to an aqueous solution of polyvinyl alcohol in amount of about 2.8% of the polyvinyl alcohol spinning solution. The resulting solution was wet spun as described in Example I. After drying the resulting fiber had a 1.1% by weight nitrogen content.

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The fiber was drawn to 3 times its length in 5 seconds at 235° C., and then heat treated at constant length for 10 seconds at 240° C. The fiber was then acetalized in an aqueous solution containing 15% sulfuric acid, 15% sodium sulfate and 5% formaldehyde for 1 hour at 70° C. The degree of acetalization was 36%.

The fiber thus obtained underwent very little shrinkage in boiling water. The fiber had dry tenacity of 6.4 grams per denier, and dry elongation of 22%. The fiber was dyed under the same conditions shown in Example I. Direct dye bath exhaustion was 100%, and acid dye bath exhaustion was 64%.

Example V

About 195 grams of 1,3-dichloro-2-hydroxypropane were added to 500 grams of 28% by weight aqueous solution of ammonia. After an exothermic reaction, the mixture is concentrated by evaporation to complete the reaction and to obtain the white-wax-like water soluble polymeric product. The polymeric amino-alcohol obtained had a nitrogen content of 18.8% by weight and a molecular weight in the range 200–1500.

The polymer was added to an aqueous polyvinyl alcohol spinning solution in amount of about 0.8% the spinning solution. The resulting solution was wet spun as described in Example I. The resulting oriented fiber was heat treated at constant length for 10 seconds at 230° C.

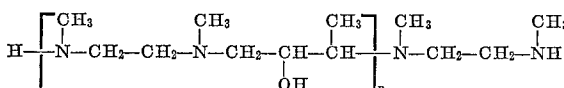
The fiber was then acetalized in an aqueous solution containing 10% sulfuric acid, 5% formaldehyde, and 15% sodium sulfate at 70° C. for 1 hour. Degree of acetalization was 32%.

When dyed as described in Example I, direct dye bath exhaustion was 100% and acid dye bath exhaustion was 66%.

Example VI

About 150 grams of N,N'-dimethyl-ethylenediamine and 250 grams of water were placed in a reactor equipped with a reflux condenser. About 120 grams of 2,3-epoxy-4-chlorobutane were gradually added at a temperature of 40° C. The mixture was then heated under reflux for 2 hours to complete the reaction.

The mixture was evaporated and an orange-yellow wax-like water soluble polymeric aminoalcohol was obtained having the formula



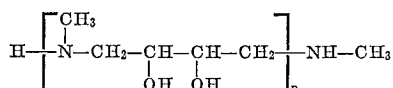
This polymer had a molecular weight in the range 200–800, and the polymer contained 13.2% by weight nitrogen.

The water soluble polymeric amino-alcohol was dissolved in aqueous polyvinyl alcohol spinning solution containing about 15% polyvinyl alcohol in amount of about 1.2% of the spinning solution. The resulting solution was wet spun as described in Example I. The oriented fiber was heat treated and acetalized as described in Example V to an acetalization degree of 33%.

The resulting fiber had excellent dyeing properties.

Example VII

About 200 grams of a 30% by weight aqueous solution of methyl amine were heated to 40° C. in a reactor equipped with a reflux condenser. About 88 grams of butadiene diepoxide were added with stirring. The resulting solution was heated under constant reflux for about 4 hours. After completion of the reaction, the solution was evaporated and a slightly yellow water soluble polymeric amino-alcohol was obtained having the formula



This polymer had a molecular weight in the range 200–800, and the polymer contained about 11.2% by weight nitrogen.

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The water soluble polymeric aminoalcohol was dissolved in aqueous polyvinyl alcohol spinning solution containing about 15% polyvinyl alcohol in amount of about 2% of the spinning solution. The resulting solution was wet spun as described in Example I.

After spinning, the resulting fiber was drawn to 2.2 times its length in 5 seconds in air at 230° C. The fiber was then heat treated at constant length for 10 seconds at 235° C.

The fiber was acetalized for 2 hours at 70° C. in an aqueous solution containing 2% sulfuric acid, 10% sodium sulfate, and 0.15% terephthalic aldehyde. The degree of acetalization was 8.2%. The resulting fiber underwent substantially no shrinkage in boiling water.

The fiber dyeability was tested by dyeing in a bath containing Chrysophenine G (Colour Index No. 24895) in amount of 2% by weight of fiber. Dye bath exhaustion was 100%.

By way of comparison with polyvinyl alcohol containing no additional polymer, which is spun and treated as above described, dye bath exhaustion was only 3.7%.

Example VIII

Polyvinyl alcohol in amount of 100 grams and 20 grams of a polymeric amine having a nitrogen content of 0.807% by weight were dissolved in water to form a solution having a 15% by weight polymer content. The polymeric amine was prepared by saponifying a copolymer of 97.5 mol percent vinyl acetate and 2.5 mol percent 5-ethyl-2-vinyl pyridine having a degree of polymerization of 33. About 10 grams of polymeric ethylenimine having molecular weight of about 1500 were dissolved in the solution.

The solution was wet spun as described in Example I. After drying the nitrogen content of the resulting fiber was 2.8% by weight.

The fiber was drawn to 2.6 times its length in 5 seconds in air having a temperature of 235° C. The fiber was then heat treated at constant length for 10 seconds at 240° C.

Subsequently, the fiber was acetalized at 70° C. for 1 hour in an aqueous solution containing 12% sulfuric acid, 15% sodium sulfate and 5% formaldehyde. The resulting fiber did not shrink substantially in boiling water.

When dyed in a dyeing bath containing 2% by weight of fiber of direct color or 4% by weight of fiber of acid color at 80° C. for 1 hour, the fiber completely exhausted the dye baths.

Example IX

Polyvinyl alcohol in amount of 405 grams was admixed with 47 grams of water soluble hydrogen chloride salt of polyvinyl amine of about 2300 molecular weight, and the resultant mixture was dissolved in 840 grams of water.

The resulting solution was extruded through a spinneret the jet of which had 30 holes each of 5.0 mm. diameter into hot air.

After dyeing the resulting fiber comprises 1.8% by weight of nitrogen. The fiber was hot drawn at 210° C. to about 8 times its original length. Subsequently, the fiber was heat treated in a molten Wood's metal bath at a temperature of 220° C. during which time the fiber underwent 15% shrinkage.

The fiber was acetalized to an acetalization degree of 33% in an aqueous bath consisting of 12% sulfuric acid, 10% sodium sulfate and 5% formaldehyde at 70° C. for 1 hour. The fiber thus obtained had good hot water resistance and good dyeability.

The dye-absorption of the fiber was tested by measuring dye bath exhaustion using a direct color dye, Nippon Fast Violet (Colour Index No. 27905), 2% by weight of fiber and an acid colour dye. Acid Brilliant Scarlet 3R7 (Colour Index No. 16255), 4% by weight of fiber. The fiber prepared by this invention completely exhausted the direct colour and exhausted about 70% of the acidic colour. Under similar conditions, normal polyvinyl al-

cohol fiber exhausts only 5% of the direct colour and 0% of the acid color.

Example X

Polyvinyl alcohol in amount of 150 grams and 18 grams of poly(2-vinyl pyridine hydrogen chloride salt) having a degree of polymerization of 1000 were dissolved in 910 grams of water.

The resulting solution was wet spun by extrusion into a substantially saturated solution of sodium sulfate. The nitrogen content of the fiber after drying was 0.45%.

The fiber was drawn to 1.8 times its initial length in 5 seconds in air having a temperature of 235° C. Subsequently the fiber was treated for 10 seconds in 240° C. air whereby the fiber underwent 20% shrinkage.

The fiber was then acetalized to a 33% degree of acetalization in an aqueous bath consisting of 12% sulfuric acid, 15% sodium sulfate and 5% formaldehyde at 70° C. for 1 hour. The resulting fiber did not shrink substantially in boiling water.

The dye absorption of the fiber was tested in a manner similar to that described in Example IX. The fiber exhausted 100% of the acid colour and 70% of the direct colour.

Example XI

A mixture of 50 grams succinic acid, 100 grams of a 60% by weight solution of hydrazine hydrate, and 0.8 gram of acetamide was heated 10 hours at 200° C. in an autoclave and then 2 hours at 270° C. The reaction mixture was dialyzed and concentrated to a 50% solution, of the resulting polyaminotriazole which had molecular weight of about 5200.

The polyaminotriazole solution was dissolved in aqueous polyvinyl alcohol spinning solution in amount of about 2.6% of the spinning solution. The resulting solution was wet spun as described in Example I. After drying, the fiber thereby obtained had a nitrogen content by weight of 4.02%.

The fiber was oriented and heat treated at constant length for 10 seconds at 235° C. in air. Subsequently the fiber was acetalized to a degree of acetalization of 32% in an aqueous bath containing 12% sulfuric acid, 15% sodium sulfate, and 5% formaldehyde.

The fiber dyeability was tested by dyeing in a bath containing Chrysophenine G (Colour Index No. 24895) in amount of 2% by weight of the fiber for 1 hour at 80° C. Dye bath exhaustion was 100%.

By way of comparison fiber prepared from just polyvinyl alcohol and treated similarly exhausts only 40% of the dye bath.

Example XII

A spinning solution containing 15% polymer was prepared. The polymer consisted of 150 grams of polyvinyl alcohol and 4 grams of amino-acetalized polyvinyl alcohol containing 2.8% by weight nitrogen which was prepared by reacting cyclo-hexylaminobutyraldehyde dimethyl acetal with polyvinyl alcohol in the presence of sulfuric acid catalyst. About 20 grams of water soluble polyvinyl pyrrolidone having molecular weight of about 9000 was added to the spinning solution.

The solution was wet spun as described in Example I. After drying, a fiber containing about 1.7% by weight nitrogen was obtained. The fiber was stretched to 2.5 times its length in 5 seconds at 235° C. and then heat treated 10 seconds at 240° C. whereby the fiber underwent 15% shrinkage.

The fiber was acetalized to a degree of acetalization of 32% in an aqueous bath containing 12% sulfuric acid, 15% sodium sulfate, and 5% formaldehyde at 70° C. for 1 hour. The fiber underwent almost no shrinkage in boiling water.

When dyed under the same conditions as described in Example I, bath exhaustion was almost 100%.

By way of comparison, with fiber prepared as above

indicated but containing no polyvinyl pyrrolidone, direct dye absorption was 73% and acidic dye absorption 53%.

Example XIII

To a 15% by weight aqueous spinning solution of polyvinyl alcohol was added 3% of water soluble polyvinyl pyrrolidone having a molecular weight of about 10,000.

The solution was wet spun as described in Example I. The oriented fiber was heat treated at constant length for 10 seconds at 240° C. The fiber was then dyed for 1 hour at 60° C. in a bath containing 2% by weight of the fiber of an acid dye, Tartrazine (Colour Index No. 19140). Dye bath exhaustion was 100%. The fiber did not shrink during dyeing.

Subsequently, the fiber was acetalized to a degree of acetalization of 21% in an aqueous solution containing 4% sulfuric acid, 2% benzaldehyde and 0.3% of an emulsifying agent in 1 hour at 70° C.

No color fading resulted from the acetalization. The fiber underwent almost no shrinkage in boiling water.

By way of comparison, with fiber containing just polyvinyl alcohol prepared as above, substantially no dye absorption takes place.

Example XIV

Polyvinyl pyrrolidone having a molecular weight of about 40,000 was dissolved in a 15% by weight solution of polyvinyl alcohol. The polyvinyl pyrrolidone was added in amount of 5% by weight of the polyvinyl alcohol solution.

The resulting solution was wet spun under conditions similar to those described in Example I. The fiber thus obtained was stretched to twice its original length at 235° C. for 1 min., and heat treated at 240° C. for 1 min. during which treatment the fiber underwent 15% shrinkage. A pure white filament containing 0.6% by weight nitrogen (2.0 mol percent vinyl pyrrolidone units) was obtained.

The fiber was acetalized for 1 hour at 70° C. in an aqueous bath of 5% formaldehyde, 15% sulfuric acid and 15% sodium sulfate to an acetalization degree of 38%. The fiber showed almost no shrinkage in boiling water and had a dry tenacity of 6.8 grams per denier and a wet tenacity of 5.5 grams per denier.

The fiber was dyed 1 hour at 80° C. using Sulfur Blue TFB (Colour Index No. 53340), 5% by weight of fiber, and 5% sodium sulfide. After oxidation and soaping had been carried out the fiber dyeability was comparable to that of cotton and viscose rayon staple.

By way of comparison, polyvinyl alcohol which had been cyanoethylated to a degree of 30 mol percent was added to regular polyvinyl alcohol in amount of 50% of the regular polyvinyl alcohol. The resulting mixture was spun, after treated and dyed in a manner similar to that described above. Dyeability of this fiber was far below that of cotton and viscose rayon staple.

Example XV

Vinyl acetate, 75.3 grams, and vinyl pyrrolidone, 32.5 grams, were copolymerized 1 hour at 60° C. under a nitrogen atmosphere using 0.5% azobisisobutyronitrile as catalyst initiator. About 60% of the monomer mixture was polymerized.

The copolymer was dissolved in water and dialyzed. The copolymer comprised 32.8 mol percent vinyl pyrrolidone units and contained 4.86% by weight nitrogen.

The copolymer was admixed with polyvinyl alcohol to produce about a 15% polymer solution, said polymer containing an average of about 1.5 mol percent vinyl pyrrolidone units.

The solution was wet spun as described in Example I. The oriented fiber was heat treated at 235° C. for 2 minutes in air. The fiber was acetalized to an acetalization degree of 43% in a 60° C. aqueous solution containing 5% formaldehyde, 15% sulfuric acid and 10% sodium sulfate for 1 hour. The resulting fiber underwent almost no shrinkage in boiling water.

The fiber was dyed 1 hour at 80° C. in a bath containing vat dye Indanthrene Blue RSN (Colour Index No. 69800) in amount of 2% by weight of fiber, 6 cc. per liter 40° Bé. sodium hydroxide and 6 grams per liter sodium hydrosulfite. After oxidation and soaping, the fiber had a clear dark blue fast color. Complete dye absorption was obtained.

By comparison, a formalized polyvinyl alcohol, degree of acetalization 12%, was mixed with polyvinyl alcohol so that the average degree of acetalization of the mixture was 6%. This mixture was spun and treated as above indicated. The fiber obtained was acetalized to a total degree of acetalization of 46%. The resulting fiber had poor hot water resistance, shrinking 16% in boiling water for 30 min., and could not be adequately dyed but only slightly stained.

Example XVI

Poly (1-vinyl-5-methyl pyrrolidone) having intrinsic viscosity of 0.03 was dissolved in about a 15% by weight solution of polyvinyl alcohol. The poly (1-vinyl-5-methyl pyrrolidone) was added in amount of about 20% by weight of the polyvinyl alcohol. The resulting solution was wet spun as described in Example I. The oriented fiber was heat treated at 235° C. for 2 min. in air.

The fiber was acetalized to an acetalization degree of 20.1% in an aqueous bath at 70° C. containing 1% benzaldehyde, 4% sulfuric acid, and 0.3% dodecyl-3-methyl ammonium chloride. The fiber thus obtained had a dry tenacity of 3.1 grams per denier, and a wet tenacity of 2.5 grams per denier. The fiber underwent 7% shrinkage when immersed for 30 min. in boiling water.

When dyed in vat dye Indanthrene Brilliant Green B (Colour Index No. 59825) under conditions similar to those above in Example XV except at 90° C., the fiber dyed to a dark clear color. The dyed fiber was extremely dye fast as against sunlight, abrasion and laundering.

Plain polyvinyl alcohol fiber prepared and treated as above indicated but without the addition of poly (1-vinyl-5-methyl pyrrolidone) could not be satisfactorily dyed.

Example XVII

When the spun fiber of Example XVI is heat drawn, heat treated, and acetalized as described in Example XIV to an acetalization degree of 40%, the fibers have a dry tenacity of 5.8 grams per denier, and a wet tenacity of 4.3 grams per denier. When immersed in boiling water for 30 min. the fiber underwent 5% shrinkage.

When dyed under the same conditions as described in Example XIV the fiber dyeability far surpassed that of cotton and viscose.

Example XVIII

About 6 cc. of a 30% hydrogen peroxide solution were added to 1,000 grams of an aqueous solution containing 111 grams vinyl pyrrolidone and 71 grams acrylamide. The mixture was copolymerized 10 hours at 60° C. Monomer to polymer conversion was about 91% and the resulting water soluble copolymer comprised about 47 mol percent vinyl pyrrolidone.

After dialysis, 100 grams of a 15% by weight solution of the copolymer were added to 1,000 grams of a 15% by weight solution of polyvinyl alcohol. The resulting solution was wet spun under conditions similar to those described in Example I. The fiber was heat stretched, heat treated and acetalized as described in Example XIV to an acetalization degree of 34%. The fiber underwent very little shrinkage in boiling water and had a dry softening point in air of 220° C.

When dyed under conditions as described in Example XIV the fiber was dyed a fast dark blue color.

By way of comparison, when polyacrylamide of intrinsic viscosity 0.05 was substituted for the copolymer used above and a fiber prepared in similar manner, the fiber dyed only to a light color.

Example XIX

About 400 grams of vinyl acetate and 6.2 grams of 5-ethyl-2-vinyl pyridine were polymerized at 60° C. under a nitrogen atmosphere using 0.5% azobisisobutyronitrile as catalyst. After 13 hours an additional 5 grams of 5-ethyl-2-vinyl pyridine was added. Subsequently at 6 hour intervals three more 5 gram portions of 5-ethyl-2-vinyl pyridine were added.

About 150 grams of polymer product were obtained. The polymer was saponified, and a water soluble copolymer product containing 0.38% by weight of nitrogen (2,3 mol percent 5-ethyl-2-vinyl pyridine) was obtained.

About 20 grams of the copolymer and 10.5 grams of polyvinyl alcohol were dissolved to form a 15% by weight aqueous spinning solution. The solution was spun as described in Example I. After drying, a fiber containing 0.24% by weight of nitrogen was obtained.

The oriented fiber was heat treated at 240° C. for 5 seconds and acetalized to a 40% degree of acetalization in aqueous solution containing 12% sulfuric acid, 15% sodium sulfate and 5% formaldehyde.

The fiber thus obtained shrinks 7% of the length after 1 hour in boiling water and has a dry softening point of 190° C. Dry tenacity was 3.5 grams per denier and dry elongation was 32%.

When dyed under the same conditions as described in Example I, acid dye bath exhaustion was almost 100% while direct dye bath exhaustion was 63%.

By way of comparison, fiber containing just polyvinyl alcohol treated as above with degree of acetalization of 34%, had dry tenacity of 3.8 grams per denier and dry elongation of 29%. Acid dye bath exhaustion was 0% and direct dye bath exhaustion was 15%.

We claim:

1. An oriented fiber having improved dyeability comprising a blend of at least 30% by weight of a vinyl alcohol polymer selected from the group consisting of polyvinyl alcohol containing vinyl alcohol units and a vinyl alcohol polymer, containing vinyl alcohol units and acetalized vinyl alcohol units, in uniform admixture with a nitrogen-containing water-soluble polymer, in a quantity to impart to the fiber a nitrogen content in the range of 0.1 to 5% by weight based on the quantity of vinyl alcohol units in said vinyl alcohol polymer, said water-soluble nitrogen-containing polymers being selected from the group consisting of water-soluble polycondensation products of an epihalohydrin and ammonia, water-soluble polycondensation products of epihalohydrin and a primary amine, water-soluble polycondensation products of an epihalohydrin and a di-secondary amine, water-soluble polycondensation products of a dihalohydrin and ammonia, water-soluble polycondensation products of a dihalohydrin and a primary amine, water-soluble polycondensation products of a dihalohydrin and a di-secondary amine, water-soluble polycondensation products of a diepoxide and ammonia, water-soluble polycondensation products of a diepoxide and a primary amine, water-soluble polycondensation products of a diepoxide and a di-secondary amine, water-soluble polymeric alkylenimines, homopolymers of allyl amine, copolymers of allyl amine and vinyl acetate, homopolymers of vinyl pyridine, copolymers of vinyl pyridine and vinyl acetate, homopolymers of an alkyl substituted vinyl pyridine, copolymers of an alkyl substituted vinyl pyridine and vinyl acetate, water soluble polyaminotriazoles, homopolymers of vinyl pyrrolidone, copolymers of vinyl pyrrolidone and vinyl acetate, homopolymers of an alkyl substituted vinyl pyrrolidone, and copolymers of an alkyl substituted vinyl pyrrolidone and vinyl acetate.

2. The oriented fiber of claim 1 wherein the water-soluble nitrogen-containing polymer is a homopolymer of vinyl pyridine.

3. The oriented fiber of claim 1 wherein the water-solu-

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ble nitrogen-containing polymer is a homopolymer of vinyl pyrrolidone.

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