

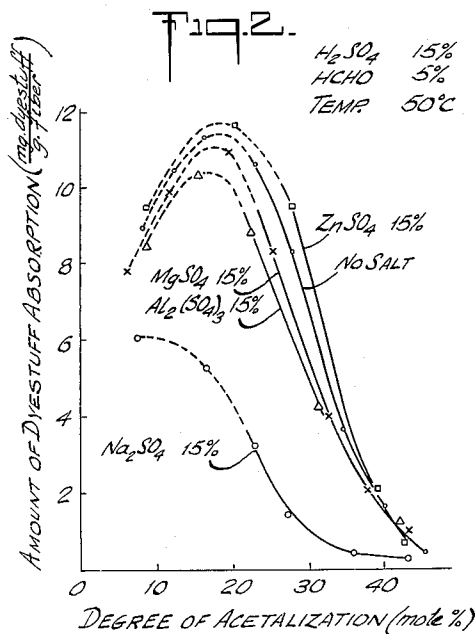
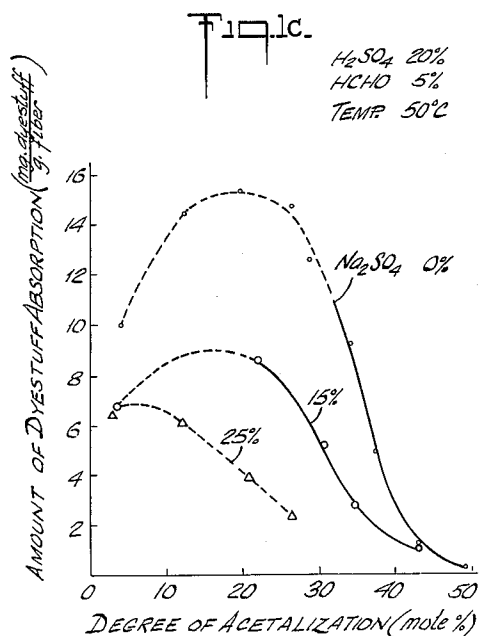
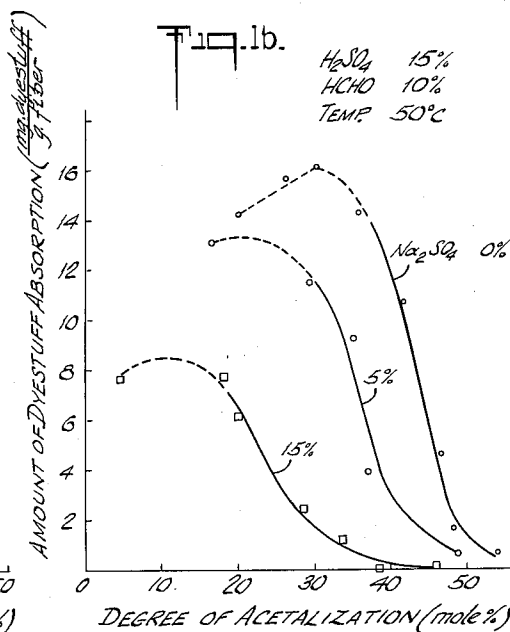
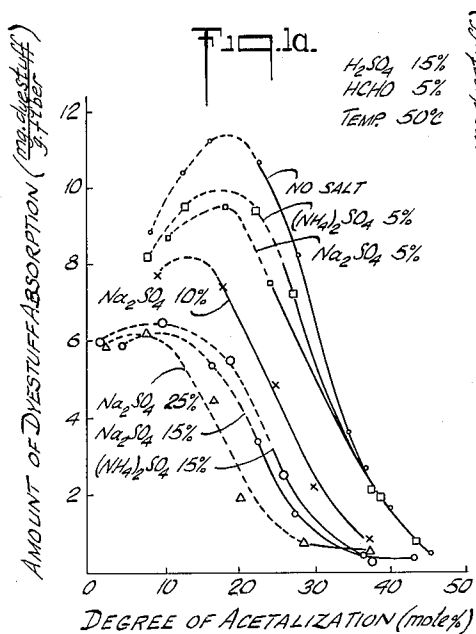
March 28, 1961

TETSURO OSUGI ET AL
PROCESS OF IMPROVING THE DYEING PROPERTIES
OF POLYVINYL ALCOHOL FIBERS

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Filed Dec. 19, 1952

2 Sheets-Sheet 1



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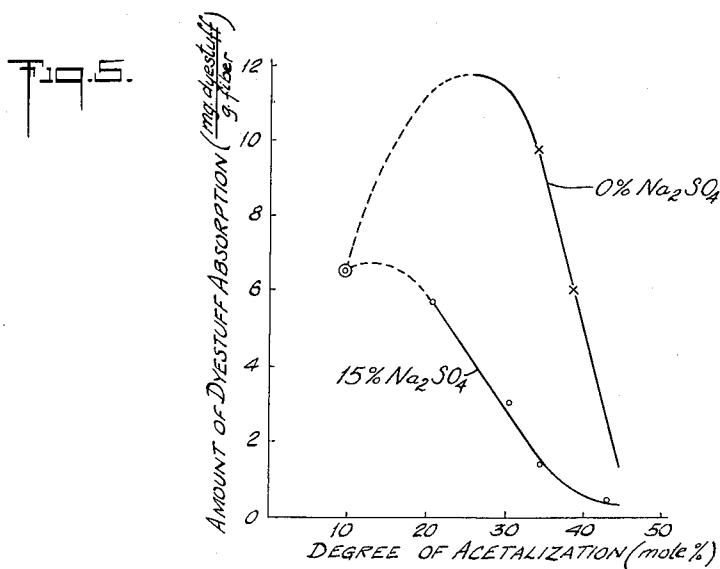
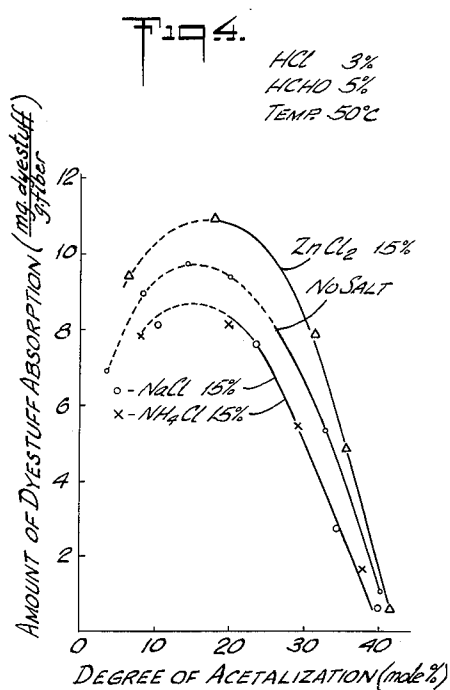
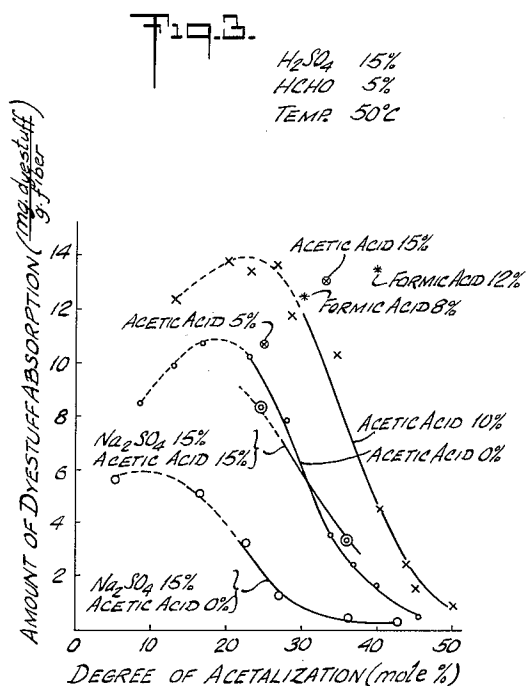
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2,977,183

PROCESS OF IMPROVING THE DYEING PROPERTIES OF POLYVINYL ALCOHOL FIBERS

Tetsuro Osugi, Kenichi Tanabe, and Osamu Morimoto, Kurashika-shi, Japan, assignors, by direct and mesne assignments, of one-fourth to Air Reduction Company, Incorporated, New York, N.Y., a corporation of New York, and three-fourths to Kurashiki Rayon Co., Ltd., Okayama Prefecture, Japan, a corporation of Japan

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Claims priority, application Japan Dec. 19, 1951

6 Claims. (Cl. 18—54)

The invention relates to a process for improving the dyeing properties of polyvinyl alcohol fibers and rendering the same resistant to boiling water.

Polyvinyl alcohol fibers as obtained by dry or wet spinning methods from aqueous polyvinyl alcohol solutions shrink considerably in water at room temperature and dissolve in hot water at 60 to 80° C.; they are, therefore, unsuited for textile purposes and have to be subjected to an after-treatment in order to increase their water resistance.

One of the best known methods for insolubilizing polyvinyl alcohol in hot or boiling water is by acetalization with formaldehyde. Another method whereby polyvinyl alcohol fibers are not only insolubilized but also made unshrinkable in boiling water consists in subjecting polyvinyl alcohol fibers, prior to their acetalization, to a heat treatment at temperatures of 140 to 225° C., preferably in an unsaturated atmosphere of water or alcohol vapors, as disclosed in the compending applications for patent by Tsukumo Tomonari and Shigeki Nomura, Serial Nos. 154,873 and 300,375, filed April 8, 1950, and July 23, 1952, respectively.

By said heat treatment the softening temperature, i.e. the temperature at which the fiber shrinks 5% of its length in water is raised to 80–96° C., and the subsequent acetalization raises the softening point further to above 100° C.

When a water-sensitive polyvinyl alcohol fiber is directly acetalized after spinning without the heat treatment referred to hereinabove, the fiber shrinks more than 10 percent of its length during the acetalization and the fibers tend to stick together after drying unless the acetalization bath contains a large amount of a strong coagulating agent for polyvinyl alcohol. Therefore, the conventional acetalizing solutions contain a powerful coagulating agent such as sodium or ammonium sulfate in an amount of at least 15 percent.

While the combination of heat treatment and subsequent acetalization according to the above-mentioned method accomplishes the desired aim of making polyvinyl alcohol fibers resistant to boiling water, it has the drawback of reducing considerably the affinity of the polyvinyl alcohol fibers to dyestuffs, particularly to direct dyestuffs. It has been extremely difficult to dye heat-treated and then partially acetalized polyvinyl alcohol fibers under normal dyeing conditions to medium or heavy shades. This is true of direct, basic, acid, sulfide, vat, naphthol and even acetate dyestuffs.

It is, therefore, a principal object of the invention to provide an acetalization method which imparts to polyvinyl alcohol fibers a sufficient resistance to boiling water but is not accompanied by a decrease of the affinity of the fibers to dyestuffs.

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

As pointed out hereinabove, it is necessary to add alkali metal or ammonium salts in an amount of at least

15 percent to the formaldehyde solutions used for the direct acetalization of freshly spun water sensitive polyvinyl alcohol fibers.

We have found that in acetalizing polyvinyl alcohol fibers which already have a high softening point of at least 80° C. it is not necessary to use such high concentrations of salt such as sodium or ammonium sulfate and that, on the contrary, the use of acetalizing baths having much lower concentrations of the salt than employed heretofore results in a surprising and unexpected increase of the dyestuff affinity of the fiber.

The acetalizing bath according to our invention contains an aldehyde, or a compound giving off aldehyde in the presence of acid, in the conventional concentration of 0.5 to 15 percent, preferably 2 to 8 percent, an inorganic acid in a concentration of about 0.5 to 25 percent, and as critical feature an alkali metal or ammonium salt in a concentration of less than 5 percent, all figures given by weight.

The obtained acetalization degree depends on the composition of the acetalizing bath, on the reaction temperature and time as well as on the properties of the treated polyvinyl alcohol fiber. The use of higher concentrations of acid or aldehyde, and also the use of higher temperatures, result in greater degrees of acetalization. The effect of the salt concentration on the degree of acetalization is generally small, but the extent of the preceding heat-treatment exerts a certain influence on the acetalization degree insofar as the higher the softening point (in water) of the heat-treated polyvinyl alcohol fiber is, the slower is the rate of acetalization. But this difference is rather small in the here interesting softening point range (in water) between 80° C. and 96° C. The effect of the fiber diameter is noticeable, but can be disregarded for fibers having 1–20 denier.

The preferred aldehydes are lower aliphatic aldehydes or compounds yielding such aldehydes or decomposable thereto by acids, such as their polymers and amination products. Examples are formaldehyde, paraformaldehyde, polyoxymethylene, hexamethylenetetramine, acetaldehyde, paraldehyde, and the like. As the inorganic acid, we prefer to use sulfuric acid, but other acids such as hydrochloric acid or even phosphoric or nitric acid can also be used. If sulfuric acid is replaced by such other acid, the concentration of, for instance, hydrochloric acid should be generally somewhat lower, and that of phosphoric acid somewhat higher, than the concentration of the sulfuric acid. As inorganic salt we employ preferably a salt or a mixture of salts of the acid used, in the case of sulfuric acid, for instance, sodium sulfate and/or ammonium sulfate.

When the polyvinyl alcohol fiber has been prepared by spinning a polyvinyl alcohol solution into a coagulating bath containing an inorganic salt such as sodium or ammonium sulfate, a certain amount of said salt will adhere to the fiber and will be carried therewith into the acetalizing bath. This amount has to be taken into account in adjusting the concentration of the acetalizing bath. The introduction of such adhering salts in amounts sufficient to raise the salt content of the acetalizing bath above 5% by weight should be avoided.

Accordingly, it is often necessary to decrease the salt content of such fibers before they pass into the acetalization bath. In general, it is difficult to remove the salt completely from the fiber but it is quite easy to reduce the salt content of the fiber to 5 to 10 percent, based on the weight of the dry fiber.

When the fiber is washed before the heat-treatment, it is necessary to leave at least 5 to 10% of salt on the fiber in order to insure that the filaments do not stick together during drying and do not become discolored

in the heat-treating step. The heat-treated fiber can be washed to a salt content of less than 5 percent, but it takes a very long time to wash out the salt completely. When the heat-treated fiber is washed with water to a salt content of less than 10 percent and then squeezed between rolls to a moisture content of less than 200 percent, it is possible to keep the salt concentration in the acetalizing bath at the desired proportion of less than 5 percent.

The concentration of the inorganic acid in the acetalizing bath has a little influence on the dyeing properties of the acetalized fibers. Higher concentrations, however, may affect the mechanical properties of the fiber. Sulfuric acid, for instance, tends to decrease the tensile strength of the fiber when present in concentrations above 20 percent, and in concentrations of 25 to 30 percent it may solubilize the fiber in the acetalization bath. But we found that an addition of organic acids having not more than 5 carbon atoms considerably increases the affinity of the fibers to dyestuffs without substantially affecting their mechanical properties. Such acids are, for instance, formic acid, acetic acid, propionic acid, butyric acid, monochloroacetic acid, glycolic acid, lactic acid, and others; they may be added in amounts up to 20 percent based on the weight of the acetalizing bath.

A modification of our new process consists in carrying out the acetalization in two steps. In the first step, the fiber is acetalized in a conventional acetalization bath to an acetalization degree of less than 20 percent; the second and final acetalization step is carried out in an acetalizing bath according to our invention, i.e. in a bath containing less than 5 percent of alkali metal or ammonium salts, and, if desired, an organic acid.

The relationship between the acetalizing bath composition, acetalization degree and dyestuff absorption is shown, by way of example, by the graphs in the accompanying drawing, in which

Figs. 1a-1c show the absorption of dyestuffs as a function of the acetalization degree obtained in solutions containing varying amounts of sulfuric acid, formaldehyde and sodium or ammonium sulfate;

Fig. 2 is a graph showing the effect of additions of inorganic sulfates other than sodium or ammonium sulfate;

Fig. 3 is a graph showing the influence of additions of organic acids;

Fig. 4 is a similar graph showing the influence of various chlorides added to an acetalization bath containing hydrochloric acid; and

Fig. 5 illustrates a two-step acetalization process.

The polyvinyl alcohol fibers used for these tests had been heated according to the method disclosed in the copending application Serial No. 300,375, recited above, for 5 minutes in super-heated steam of 200° C. with a water vapor pressure of 2.3 atm. abs. and had been washed with water at room temperature so as to remove substantially the sodium sulfate adhered to the fibers. The fibers had a softening temperature in water (as defined hereinabove) of 85° C. The different acetalization degrees of the fibers were obtained by proper control of the acetalization time.

As will be noted on inspection of Fig. 1, the dyestuff absorption increases with decreasing sodium or ammonium sulfate content of the acetalization bath. For each salt concentration, the dyestuff absorption decreases generally, in the range of higher acetalization degrees, with increasing acetalization. This would suggest a procedure to acetalize the fibers as little as possible. However, a higher acetalization degree is necessary to obtain a high wet-heat resistance of the fibers. This is indicated by the dotted and solid parts of the curves. The dotted sections designate the range where the fibers shrink in water of 100° C. by more than 5 percent, i.e. where they have an insufficient wet-heat resistance. The range where the fibers do not shrink more than 5 percent at 100° C. is

designated by the solid sections, and it will be noted that this range corresponds in almost all cases to a minimum acetalization degree of at least 20 percent, i.e. where at least 20 percent of the original hydroxyl groups of the polyvinyl alcohol are acetalized. On the other hand, too high a degree of acetalization is also objectionable because highly acetalized polyvinyl alcohol has a low heat resistance in air. The acetalization degree should be about 25 to at most 50 percent.

The acetalizing solutions used in the tests of Fig. 1a contained by weight 5 percent of formaldehyde, 15 percent of sulfuric acid and 0, 5, 15, and 25 percent of sodium sulfate, or 5 and 15 percent of ammonium sulfate, respectively.

In Fig. 1b, the formaldehyde content was raised to 10 percent, and in Fig. 1c the sulfuric acid content was raised to 20 percent.

The acetalization was in all cases carried out at 50° C. for times sufficient to obtain the indicated acetalization degrees.

The dyestuff absorption is expressed in mg. of the dyestuff Direct Fast Violet BB conc. (Color Index No. 325) absorbed within 1 hour at 70° C. by 1 g. of fiber from 30 cc. of a solution containing 2 percent of the dyestuff, based on the weight of the fiber.

The dyestuff absorption of cotton is about 10 mg./g. fiber and that of viscose rayon about 15 mg./g. fiber. The graph shows that the dyestuff absorption of polyvinyl alcohol fibers is comparable with that of cotton and viscose rayon, if the polyvinyl alcohol fiber has been acetalized with acetalizing solutions containing not more than 5 percent of sodium or ammonium sulfate.

Similar figures for the dyestuff absorption are obtained when other dyestuffs are used, such as sulfide, vat, naphthol, acid, mordant, basic, and acetate dyestuffs.

The graph of Fig. 2 shows that salts of sulfuric acid other than alkali metal or ammonium sulfate have smaller effects on the dyeing properties of the acetalized polyvinyl alcohol fibers; the effect of zinc sulfate is the least noticeable, that of magnesium sulfate is small and that of aluminium sulfate is a little more pronounced. The other sulfates, for example, the sulfates of cadmium, chrome, iron, copper or manganese have little effect, and only potassium sulfate behaves like sodium sulfate.

The graph of Fig. 3 is similar to that of Fig. 1 and illustrates the favorable influence of organic acids on the dyeing properties of the acetalized polyvinyl alcohol fiber. It will be noted that fibers acetalized in the presence of acetic and formic acid have an affinity to the dyestuff which is greater than that of cotton and about equal to that of viscose rayon.

The graph of Fig. 4 is similar to the preceding figures and illustrates the influence of the various chlorides (sodium chloride, ammonium chloride, and zinc chloride) added to the acetalization bath containing hydrochloric acid on the dyeing properties of the acetalized polyvinyl alcohol fiber.

In the tests of Fig. 5, the fiber was first acetalized at 50° C. for 10 minutes to an acetalization degree of 10 percent in a bath containing by weight 15 percent of sulfuric acid, 5 percent of formaldehyde and 15 percent of sodium sulfate. The acetalization was then continued on the one hand in a bath containing 15 percent of sulfuric acid, 15 percent of formaldehyde, and 15 percent of sodium sulfate, and on the other hand in a bath containing only 15 percent of sulfuric acid and 15 percent of formaldehyde. The curves demonstrate clearly the superiority of the after-acetalization with solutions containing less than 5 percent of the salt. We have further found that similar results as described hereinbefore are obtained when hydrochloric acid is used instead of sulfuric acid.

The following illustrative examples are given, without in any way limiting the invention, to show methods of acetalizing polyvinyl alcohol fibers without impairing

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their dyeing properties. In the examples the salt adhering to the polyvinyl alcohol fibers was not removed except where particularly noted; such an excess of acetalizing bath with respect to the amount of treated fibers was used that the concentration changes caused by the salt carried by the fibers were negligible.

All figures are given by weight.

Example 1

An aqueous polyvinyl alcohol solution was spun into a coagulating bath containing sodium sulfate; the obtained fiber was stretched during and after spinning, dried and heated in superheated steam of 220° C. at a vapor pressure of 2 atm. for a time of 5 min. The fiber, which had a softening temperature (in water) of 90° C., was acetalized at 50° C. for one hour in a bath containing 3 percent of formaldehyde, 3 percent of sodium sulfate and 14 percent of sulfuric acid.

The obtained fiber had an acetalization degree of 30 percent. When dyed at a goods-liquor ratio of 1:100 in a bath containing 5 percent of Direct Black GX (Color Index No. 581) at 70° C. for 1 hour, a deep black shade was produced.

When the same fiber was acetalized under the same conditions in a bath containing 15 percent of sodium sulfate (instead of 3 percent), and dyed in the same manner, only a grey shade was obtained.

The mechanical properties of the fibers are hardly influenced by the different composition of the acetalizing bath. The tensile strength of the fiber acetalized in the bath containing 3 percent of salt was 2.9 g./d., that of the fiber acetalized in the bath containing 15 percent of salt was 3 g./d.

Example 2

The heat treated fiber of Example 1 having a softening temperature of 90° C. was acetalized at 60° C. for one hour in a bath containing 4 percent of formaldehyde, 16 percent of sulfuric acid and 5 percent of sodium sulfate.

The obtained fiber, which had an acetalization degree of 37 percent, was dyed at a goods-liquor ratio of 1:100 in a bath containing 4 percent of Direct Brown M (Color Index No. 420) to a dark brown shade.

The fiber acetalized at 60° C. for one hour in a bath containing 4 percent of formaldehyde, 19 percent of sulfuric acid, and 25 percent of sodium sulfate had the same acetalization degree but could be dyed under the same conditions only to a light tan shade.

Example 3

The same fiber as in the preceding examples was acetalized at 50° C. for 1 hour in a bath containing 8 percent of polyoxymethylene, 15 percent of sulfuric acid and no salt. The obtained fiber had an acetalization degree of 37.9 percent. When it was dyed with 2 percent of Diamino Sky Blue A (Color Index No. 520) for 1 hour at 70° C., 9.2 mg. of the dyestuff were absorbed by 1 g. of the fiber.

When the same fiber was acetalized in a bath containing 8 percent of polyoxymethylene, 15 percent of sulfuric acid and 15 percent of sodium sulfate to an acetalization degree of 35 percent and dyed as before, only 4.8 mg. of the dyestuff were absorbed by 1 g. of the fiber.

Example 4

A dry spun polyvinyl alcohol fiber was heated for 5 min. in air of 215° C. to raise the softening temperature in water to 81° C. The fiber was then acetalized for 1 hour at 50° C. in a bath containing 5 percent of formaldehyde, 20 percent of sulfuric acid and no salt. The acetalized fiber, which had an acetalization degree of 40 percent, was blended with viscose rayon and could be dyed with direct colors to the same shade as the rayon fiber.

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Example 5

A dry spun polyvinyl alcohol fiber heated in air of 215° C. and having a softening temperature in water of 81° C. was acetalized for 1 hour at 50° C. in a bath containing 3 percent of formaldehyde and 3 percent of hydrochloric acid but no salt. The fiber had an acetalization degree of 35 percent and showed excellent affinity to direct dyestuffs.

Example 6

A polyvinyl alcohol fiber obtained by wet-spinning an aqueous polyvinyl alcohol solution into a coagulating bath containing ammonium sulfate was dried and heat-treated in superheated steam having a vapor pressure of 5 kg./cm.² at 160° C. for 20 min. The fiber was washed to a content of 4 percent of ammonium sulfate by passing it through water and squeezing it between rolls to a moisture content of 100 percent. The fiber was then continuously acetalized by passing it at 50° C. for 1 hour through a bath containing 2 percent of hexamethylenetetramine and 20 percent of sulfuric acid. The fiber, which on leaving the bath had an acetalization degree of 32.0 percent, was squeezed between rolls to a moisture content of 100 percent and could be dyed with the acid dyestuff Naphthylamine Black 10B (Color Index No. 246) to a deep black shade.

If the same fiber was acetalized to about the same acetalization degree in a bath containing the same amounts of hexamethylenetetramine and sulfuric acid, but in addition 15 percent of ammonium sulfate, the fiber could be dyed under the same conditions only to a light grey shade.

Example 7

A wet spun polyvinyl alcohol fiber was washed in the stretched state to a sodium sulfate content of 6.5 percent by passing it under a shower, dried to a moisture content below 5 percent and heated in air of 225° C. for 5 minutes. This fiber had a softening temperature in water of 87° C. The acetalization at 50° C. in acetalization baths of different composition gave the following results:

Bath compositions	Time in min.	Acetalization degree in percent	Dyestuff absorption, mg./g. fiber
1 { 15% H ₂ SO ₄ 5% CH ₂ O 10% CH ₂ COOH	60	34.7	10.0
2 { 15% H ₂ SO ₄ 5% CH ₂ O 15% H ₂ SO ₄	70	32.3	6.4
3 { 5% CH ₂ O 15% H ₂ SO ₄ 25% Na ₂ SO ₄	90	29.0	0.8

Example 8

The heat-treated polyvinyl alcohol fiber of Example 2 is passed into an aqueous acetalizing bath having a temperature of 50° C. and containing 3 percent of acetaldehyde and 15 percent of sulfuric acid. After half an hour the fiber has an acetalization degree of 41.0%.

If the same acetalizing bath is used with an addition of 10 percent of sodium sulfate, the acetalization degree is 37 percent.

The fiber acetalized in the first bath has a higher affinity to direct dyestuffs than the fiber acetalized in the second bath.

Example 9

A polyvinyl alcohol fiber obtained by a conventional wet spinning process is stretched by 20 percent of its original length in air of 225° C. during 5 min. The heat-treated and stretched fiber has a softening point in water of 82° C. The fiber is then immersed at 60° C. for 50 minutes in an aqueous solution containing 17 percent of sulfuric acid, 10 percent of sodium sulfate, 5 percent of formic acid and 5 percent of formaldehyde.

This formalized fiber has an acetalization degree of 39 percent.

If the same fiber is immersed under the same conditions in the same bath but not containing formic acid, the acetalization degree is 35%.

When both fibers are dyed with 2 percent of Benzobrown MC (Color Index No. 420) for 1 hour at 60° C., the fiber acetalized in the presence of formic acid obtains a much deeper shade than the fiber acetalized without formic acid, and the color depth of the former can be compared with the shade obtained in viscose staple fiber.

Example 10

A polyvinyl alcohol fiber obtained by a dry spinning process is heated for 30 minutes in superheated steam of 160° C. with a vapor pressure of 5 kg./cm.² and then acetalized in an aqueous solution containing 4 percent of hydrochloric acid, 10 percent of acetic acid, and 4 percent of formaldehyde at 50° C. for 30 min. to an acetalization degree of 38 percent. If acetalized under the same conditions without acetic acid, the acetalization degree is 32 percent. On the first fiber, Sulphur Blue R (Color Index 959) produces a much deeper shade under the same dyeing conditions than on the fiber acetalized without acetic acid.

Example 11

A polyvinyl alcohol fiber obtained by a wet spinning process is heated for 5 minutes in air of 220° C. One portion of the fibers is placed for half an hour at 50° C. in a solution (A) containing 15 percent of sulfuric acid, 10 percent of butyric acid, and 3 percent of acetaldehyde, the other portion under the same conditions in a solution (B) containing only 15 percent of sulfuric acid and 3 percent of acetaldehyde. The degree of acetalization is for fiber (A) 46%, for fiber (B) 44%. When dyed with Chromoxane Pure Blue B (Color Index No. 720), fiber (A) is dyed a much deeper shade than fiber (B).

Example 12

The heat-treated fiber of Example 10 is immersed for 15 minutes in an aqueous solution of 60° C. containing 15 percent of sulfuric acid, 5 percent of formaldehyde, and 15 percent of sodium sulfate. The fiber has then an acetalization degree of 14.5%. Portions of this slightly acetalized fiber are consequently placed for 50 minutes at 60° C. either in a solution (A) containing 15 percent of sulfuric acid, 5 percent of monochloroacetic acid, 10 percent of methanol and 10 percent of formaldehyde, or in a solution (B) of the same composition without the monochloroacetic acid. The acetalization degree of fiber (A) is 39%, that of fiber (B) 37%. When both fibers are dyed with Celliton Fast Blue FFR, fiber (A) is dyed a deeper shade than fiber (B).

Example 13

Heat-treated fibers according to Example 10 are placed for 1 hour at 50° C., either in an aqueous solution (A) containing 15 percent of sulfuric acid, 10 percent of lactic acid, and 5 percent of formaldehyde, or in a solution (B) containing only 15 percent of sulfuric acid and 5 percent of formaldehyde. When dyed with Indanthrene Blue RSN (Color Index No. 1106), fiber (A) assumes a deeper shade than fiber (B).

Example 14

Heat-treated fibers according to Example 10 are acetalized to an acetalization degree of 40 percent in an aqueous solution containing 15 percent of sulfuric acid, 5 percent of formaldehyde and 15 percent of (A) zinc sulfate, (B) ferrous sulfate, (C) magnesium sulfate, (D) aluminium sulfate, (E) ammonium sulfate, or (F) sodium sulfate and these acetalized fibers are dyed with Diamine Green B (Color Index No. 593). The most heavy shade is obtained in (A), (B) and (C) and the

medium shade at (D); (E) and (F) are only stained a very light shade.

The term "polyvinyl alcohol" as used in the specification and claims is understood to mean not only pure polyvinyl alcohol but also its copolymers with other polymerizable compounds, such as ethylene, maleic anhydride, acrylonitrile, and the like, provided such copolymers contain at least 80 percent by weight of polyvinyl alcohol. Such copolymers are known in the art and have been proposed for the preparation of textile fibers in the same way as polyvinyl alcohol.

The term "water-soluble lower aliphatic aldehyde" as used in the claims is understood to cover also compounds of such aldehydes specified above, as polymers and amination products, which split off the aldehyde in the acid solution.

What we claim is:

1. A process for improving the dyeing properties of polyvinyl alcohol fibers, the shrinkage of which has been reduced by a heat treatment to a shrinkage of not more than 5 percent of their length in water of 80° C., said process comprising treating said fibers with an aqueous solution containing by weight about .5 to 15 percent of formaldehyde, about .5 to 25 percent of an inorganic acid selected from the group consisting of hydrochloric acid and sulfuric acid, and an inorganic salt selected from the group consisting of ammonium and alkali metal salts of said acid in a concentration not exceeding 5 percent of said solution, for a time and at a temperature sufficient to acetalize about 25 to 50 percent of the hydroxyl groups of the polyvinyl alcohol.

2. A process for improving the dyeing properties of polyvinyl alcohol fibers, the shrinkage of which has been reduced by a heat treatment to a shrinkage of not more than 5 percent of their length in water of 80° C., said process comprising treating said fibers with an aqueous solution containing by weight about .5 to 15 percent of formaldehyde, about .5 to 25 percent of an inorganic acid selected from the group consisting of hydrochloric acid and sulfuric acid, an inorganic salt selected from the group consisting of ammonium and alkali metal salts of said acid in a concentration not exceeding 5 percent of said solution and about .5 to 25 percent of an alkyl carboxylic acid containing not more than 5 C atoms, for a time and at a temperature sufficient to acetalize about 25 to 50 percent of the hydroxyl groups of the polyvinyl alcohol.

3. A process for improving the dyeing properties of polyvinyl alcohol fibers comprising spinning an aqueous solution containing polyvinyl alcohol into a coagulating bath containing a coagulating salt selected from the group consisting of alkali metal and ammonium sulfates and chlorides, heating the obtained filaments to a temperature of about 140 to 225° C. until said filaments shrink less than 5 percent of their length in water of 80° C., removing the coagulating salt adhered to the filaments from the coagulating bath to such an extent that the filaments contain not more than 10 percent by weight of said salt, and treating said filaments with an aqueous acetalizing solution containing by weight about .5 to 15 percent of formaldehyde, about .5 to 25 percent of the acid of said coagulating salt, and said coagulating salt in such an amount that said salt total concentration in the solution does not exceed 5 percent, for a time and at a temperature sufficient to acetalize about 25 to 50 percent of the hydroxyl groups of the polyvinyl alcohol.

4. The process as defined in claim 3, wherein said aqueous acetalizing solution contains, in addition about .5 to 25 percent of an alkyl carboxylic acid containing not more than 5 carbon atoms.

5. A process for improving the dyeing properties of polyvinyl alcohol fibers, the shrinkage of which has been reduced by a heat treatment to a shrinkage of not more than 5 percent of their length in water of 80° C., said

process comprising first acetalizing not more than 20 percent of the hydroxyl groups of the polyvinyl alcohol with formaldehyde and then treating said acetalized fibers with an aqueous acetalizing solution containing by weight about .5 to 15 percent of formaldehyde, about .5 to 25 percent of an inorganic acid selected from the group consisting of hydrochloric acid and sulfuric acid, and an inorganic salt selected from the group consisting of ammonium and alkali metal salts of said acid in a concentration not exceeding 5 percent of said solution for a time and at a temperature sufficient to raise the total acetalization degree of the polyvinyl alcohol to about 25 to 50 percent.

6. The process as defined in claim 5, wherein said aqueous acetalizing solution contains, in addition, about .5 to 25 percent of an alkyl carboxylic acid containing not more than 5 carbon atoms.

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