PREPARATION OF POLYVINYL ALCOHOL BODIES HAVING IMPROVED KNOT STRENGTH

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This invention relates to a method of improving the properties of shaped polyvinyl alcohol bodies, particularly fibers of the polyvinyl alcohol series. It relates especially to a method of improving the knot strength of such fibers, as well as obtaining good elasticity and hot water resistivity.

It is known that polyvinyl alcohol fibers, as produced by a wet or dry spinning of polyvinyl alcohol solutions, need to be subjected to an after-treatment to obtain the properties necessary for use as all-purpose textile fibers. The best known after-treatment is the acetalization with formaldehyde or acetaldehyde, which is employed to increase the water resistance of the fibers. This acetalization treatment may be preceded by a heat treatment to improve the softening temperature in water. Although these procedures impart to polyvinyl alcohol fibers improved water resistance they have less influence on the elastic properties of the fibers.

This application is a continuation-in-part of our application Serial Number 336,021, filed February 9, 1953 now abandoned, for "Treatment of Shaped Polyvinyl Alcohol Bodies. In our parent application it was found that good elastic recovery, as well as dry and wet heat resistance, was obtained by treating the polyvinyl fibers with dialdehydes, ketoaldehydes, or acetaldehyes, and particularly by a treatment with aromatic dialdehydes, ketoaldehydes, or acetaldehyes. This treatment could replace the conventional acetalization with formaldehyde or acetaldehyde, or it could be applied together with, or in addition to, such acetalization.

The more outstanding effect of the dialdehyde treatment on the dry and wet heat resistance and the elastic recovery, rather than the treatment with monoaldehydes, such as formaldehyde and acetaldehyde, may be due to cross-linkages between polyvinyl alcohol chains, as illustrated by the following formula, using succinic aldehyde:

H₂C/H₂C
H₂—O—O—CH₂
H₂C—CH₂—CH—CH₂—CH₂—H₂C
H₂—O—O—CH₂

Although the acetalization of the parent process is a very effective method of improving heat resistivity, hot water resistivity and elasticity, the knot strength of the fiber is not increased correspondingly under all conditions described in the parent case. In fact, usually the knot strength decreases. The reduction of the knot strength was believed to be caused mainly by the non-uniform distribution of the cross-linkages in the fiber. Various experiments were, therefore, previously made with the object of distributing the cross-linkages more evenly.

A principal object of this invention is to provide a method for treating polyvinyl alcohol fibers which will produce improved hot water resistivity and elasticity, and at the same time produce improved knot strength and knot elongation.

Another object of the invention is to provide a polyvinyl alcohol type of fiber having improved physical characteristics, and being suitable as a synthetic fiber for the manufacture of textiles.

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

The present invention is based upon the discovery that, in order to obtain fibers which will have high hot water resistivity and elasticity, and at the same time have improved knot strength and knot elongation, it is necessary to have a rapid acetalization reaction which will give a relatively non-uniform distribution of the cross-linkages in the fiber. This is accomplished by treating the fiber with a dialdehyde in which the aldehyde groups are separated by at least two carbon atoms, and by using a relatively high acid catalyst concentration.

The properties of the treated fiber are controlled mainly by the degree of cross-linkage between polyvinyl alcohol chains, and the distribution of the cross-linkages. The distribution of the cross-linkages may vary with the particular fiber used.

The resistance of the treated fiber to hot water in influenced predominantly by the degree of cross-linkages, but not so much by the distribution of the cross-linkages. One of the other hand, the strength and elongation, and the knot strength and elongation of the treated fiber are affected by both the degree of cross-linkages and the distribution thereof. For example, the knot strength and elongation are greater at the same degree of cross-linkage in the case of exceedingly non-uniform distribution.

The reason for the better knot strength of the fibers in the case of non-uniform distribution of the cross-linkages is not clear. One possible explanation is that the reaction surface of the fiber is covered by a layer having a three-dimensional structure and that the strength and elongation is maintained mainly by the inner part of the polyvinyl alcohol fiber.

In order to make a non-uniform distribution of the cross-linkage, it is necessary that the rate of the cross-linkage reaction be greater than the penetrating speed of the reagent into the fiber. When this occurs the reaction is concentrated principally on the surface of the fiber. Swelling of the fiber is suppressed, and the reagent can no longer enter into the interior of the fiber. Therefore, it is necessary to select a dialdehyde which has a fast velocity of cross-linkage reaction and at the same time to select reacting conditions which accelerate this action.

Suitable dialdehydes are those in which the aldehyde groups are separated by at least two carbon atoms. The most easily accessible, and therefore preferred, dialdehydes are those which have from two to four carbon atoms between the aldehyde groups, namely, succinic dialdehyde, glutaric dialdehyde and adipic dialdehyde. Longer chain dialdehydes, such as suberic acid, and substituted dialdehydes such as a-hydroxyaldehydes may also be used. Also included are compounds hydrolyzable into such dialdehydes in situ, i.e. dialdehyde precursors, including for example, acetal and hemiacetal of the dialdehydes, and cyclic anhydrides of dihemiacetals of dialdehydes. Examples of compounds of this type are 2,5-dimethoxy- and 2,5-dihydroxymethylfurural, which hydrolyze to succinic dialdehyde. It may be preferred to use the dialdehydes in the form of their acetals, as these compounds are more stable than the free aldehydes and give excellent results. The dialdehyde, or potential dialdehyde, which may function as a cross-linking agent can be used in varying concentrations. Concentrations of about 0.39 to 2% have been found to be particularly useful.

The velocity and degree of acetalization depend not only upon the dialdehyde used, but also on the acid concentration of the acetalization bath. It is an advantage of this invention that the acetalization may be carried
out in aqueous solution, but the acid concentration of the aqueous solution must be sufficient to accelerate the acetalization reaction. Even with the use of a dialehyde in which the velocity of the cross-linkage is sufficiently fast, if the acid concentration is low, or if a reagent such as sodium hydroxide sulfite or sodium sulfite is present, which reduces the reaction velocity even though the acid concentration is high, satisfactory results are not obtained. As the inorganic acid we prefer to use sulfuric acid, but other acids such as hydrochloric or phosphoric acids can also be employed. For successful practice of this invention a sulfuric acid concentration of at least 8% must be used. Sulfuric acid concentrations up to 20% or more have been found to give excellent results. When phosphoric acid is used, a concentration of at least 10% must be employed. The catalytic action of a 2% concentration of hydrochloric acid gives an equivalent effect. The optimum acid concentration may vary with the dialdehyde, or other reagents used in the reaction.

Suitable concentrations of metal salts may be added to the bath in order to prevent excessive swelling of the fiber. If an inorganic salt is added to the bath, we use preferably a salt, or a mixture of salts, of the acid used. In the case of sulfuric acid, for instance, we prefer sodium sulfate.

As a rule higher aldehyde concentrations and higher acid concentrations increase the reaction rate. Bath temperatures are generally maintained at about 40–70°C. although not necessarily limited thereto. In order to obtain sufficient dry and wet heat resistance, good elastic recovery and good knot strength it is generally necessary that the weight increase due to acetalization is 1–20%, although the amount depends on the kind of dialdehyde used.

The method of the invention, though particularly suitable for fibers and filaments, is not limited thereto but can be applied also to tubes, envelopes, films, and other structures made of polyvinyl alcohol. The term "polyvinyl alcohol" as used throughout the specification and claims is to be understood to refer not only to polyvinyl alcohol proper but also to its copolymers with other polymerizable compounds, provided such copolymers are well known in the art contain at least 80 percent by weight of polyvinyl alcohol.

Experimental data showing the physical properties of the fibers obtained using malonic dialdehyde, glutaric dialdehyde and succinic dialdehyde with varying concentrations of sulfuric acid are shown in the following table. The fibers were subjected to the same heat treatments in each case.

### Table

<table>
<thead>
<tr>
<th>Kinds of aldehydes</th>
<th>Reaction temperature (°C)</th>
<th>Concentration of sulfuric acid (percent)</th>
<th>Degree of acetalization, a (mol percent)</th>
<th>Dry knot strength, (g/dl)</th>
<th>Knot elongation, (percent)</th>
<th>Heat and hot water resistivity, b (following points, °C)</th>
<th>Elastic recovery at 3% elongation, (percent)</th>
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</thead>
<tbody>
<tr>
<td>Malonic dialdehyde</td>
<td>70</td>
<td>10</td>
<td>13.7</td>
<td>0.38</td>
<td>1.7</td>
<td>130</td>
<td>57</td>
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<td></td>
<td>70</td>
<td>20</td>
<td>10.26</td>
<td>0.04</td>
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<td>70</td>
<td>30</td>
<td>9.65</td>
<td>0.18</td>
<td>4.6</td>
<td>100-120</td>
<td>48</td>
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<tr>
<td></td>
<td>70</td>
<td>40</td>
<td>8.67</td>
<td>0.28</td>
<td>15.1</td>
<td>110</td>
<td>51</td>
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<td></td>
<td>70</td>
<td>50</td>
<td>7.67</td>
<td>0.38</td>
<td>15.8</td>
<td>120</td>
<td>61</td>
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<tr>
<td>Glutaric dialdehyde</td>
<td>70</td>
<td>5</td>
<td>13.65</td>
<td>0.26</td>
<td>0.8</td>
<td>120-130</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>10</td>
<td>14.05</td>
<td>1.18</td>
<td>7.6</td>
<td>130-130</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>20</td>
<td>9.11</td>
<td>1.18</td>
<td>12.9</td>
<td>130-130</td>
<td>61</td>
</tr>
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<td></td>
<td>70</td>
<td>30</td>
<td>0.42</td>
<td>1.28</td>
<td>14.1</td>
<td>120-130</td>
<td>59</td>
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<td>70</td>
<td>40</td>
<td>0.20</td>
<td>1.18</td>
<td>12.9</td>
<td>130-130</td>
<td>60</td>
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<tr>
<td></td>
<td>70</td>
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<td>0.12</td>
<td>1.27</td>
<td>12.2</td>
<td>130-130</td>
<td>60</td>
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<tr>
<td>Succinic dialdehyde</td>
<td>70</td>
<td>10</td>
<td>11.45</td>
<td>0.33</td>
<td>17.7</td>
<td>120</td>
<td>50</td>
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<td></td>
<td>70</td>
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<td>12.11</td>
<td>1.18</td>
<td>14.4</td>
<td>130-130</td>
<td>60</td>
</tr>
</tbody>
</table>

1% by weight of sodium hydroxide sulfite was added to the reaction bath.

The degree of acetalization was calculated by the increase in weight of the fiber.

The softening point was determined by the temperature at which 10% contraction occurs after immersion for 1 hour.

It can be clearly seen from the table that when the polyvinyl alcohol fiber is treated in aqueous solution with an aliphatic dialdehyde in which the aldehyde groups are separated by at least two carbon atoms, e.g. succinic dialdehyde, and glutaric dialdehyde, the knot strength increases as the concentration of the sulfuric acid increases. Effective results cannot be obtained with glyoxal, nor with malonic acid dialdehyde because the velocity of the cross-linkage is slow.

The following examples are given to illustrate the method of the invention and are not intended to limit the invention in any way. All figures are given by weight.

### EXAMPLE 1

A polyvinyl alcohol fiber obtained by a conventional wet spinning process, using a polyvinyl alcohol having an average degree of polymerization of 1700 was subjected to heat treatment in air at 235°C for 3 minutes at constant length. The fiber was then treated with an aqueous solution containing 0.39% of 2,5-diethoxynitrohydrofuran, 10% sulfuric acid and 10% of sodium sulfate at 70°C for 4 hours. The fiber thus obtained showed a weight increase due to acetalization of the fiber corresponding to about 14.05 percent of the hydroxyl groups in the polyvinyl alcohol. The fiber showed almost no contraction when dipped in hot water for one hour. It showed a knot strength of 1.13 g/d. Elastic recovery was 62% after 3% elongation.

### EXAMPLE 2

A polyvinyl alcohol fiber obtained by a conventional wet spinning process, using a polyvinyl alcohol having an average degree of polymerization of 1700 was subjected to heat treatment in air at 235°C for 3 minutes at constant length, as in Example 1. The fiber was then treated with an aqueous solution containing 0.47% of glutaric dialdehyde tetramethyl acetal, 20% of sulfuric acid and 10% of sodium sulfate at 70°C for 24 hours. The fiber thus obtained showed a weight increase due to acetalization of the fiber corresponding to about 12.10% of the hydroxy groups in the polyvinyl alcohol. The knot strength was 1.27 g/d and the knot elongation was 13%. Elastic recovery was 60% after 3% elongation.

### EXAMPLE 3

A polyvinyl alcohol fiber obtained by a conventional wet spinning process, using a polyvinyl alcohol having an average degree of polymerization of 1700 was subjected to heat treatment in air at 235°C for 3 minutes at constant length, as in Example 1. The fiber was then treated with an aqueous solution containing 0.5% of 2,5-dimethoxynitrohydrofuran, 50% of sulfuric acid, and 10% of sodium sulfate at 70°C for 8 hours. The fiber thus obtained showed a weight increase due to acetalization of the fiber corresponding to about 17.5% of the hydroxyl groups in the polyvinyl alcohol. The knot strength was 1.01 g/d. The shrinkage on treatment with hot water at 130°C for one hour was about 4%. Elastic recovery was 67% after 3% elongation.
EXAMPLE 4

A polyvinyl alcohol fiber obtained by a conventional wet spinning process, using a polyvinyl alcohol having an average degree of polymerization of 1700 was subjected to heat treatment in air at 235 °C. for 3 minutes at constant length, as in Example 1. The fiber was then treated with an aqueous solution containing 0.39% of 2,5-diethoxymethylpropanol, 20% of sulfuric acid and 10% of sodium sulfate, at 40 °C. for one hour. The fiber thus obtained showed a weight increase due to acetalization of the fiber corresponding to about 4.71% of the hydroxyl groups in the polyvinyl alcohol. The knot strength was 1.88 g./d. and the elongation was 15.7%.

For comparison, a polyvinyl alcohol fiber was treated under the same conditions except that the sulfuric acid concentration was only 5%. The resulting fiber showed a weight increase due to acetalization of the fiber corresponding to only about 5.08% of the hydroxyl groups in the polyvinyl alcohol. The knot strength was only 0.86 g./d. and the knot elongation only 8.9%.

EXAMPLE 5

A polyvinyl alcohol fiber obtained by a conventional wet spinning process using polyvinyl alcohol having an average degree of polymerization of about 1700, and without heat treatment, was treated at constant length with an aqueous solution containing 1.0% of diethoxymethylpropanol and 15% of sulfuric acid. The fiber thus obtained showed a weight increase due to acetalization of the fiber corresponding to about 20.3% of the hydroxyl groups in the polyvinyl alcohol. The knot strength was 1.03 g./d.

EXAMPLE 6

A polyvinyl alcohol fiber was obtained by a conventional dry-spinning process and subjected to heat treatment. The fiber was then treated with an aqueous solution containing 0.39% of diethoxymethylpropanol, 3% of hydrochloric acid and 10% of sodium chloride at 60 °C. for 3 hours. The fiber thus obtained showed a weight increase due to acetalization of the fiber corresponding to about 10.5% of the hydroxyl groups in the polyvinyl alcohol. The knot strength was 1.21 g./d. and the knot elongation 9.8%.

EXAMPLE 7

A polyvinyl alcohol fiber was obtained by a conventional dry-spinning process and subjected to heat treatment as in Example 6. The fiber was then treated in an aqueous solution containing 2.0% of glutaric dialdehyde tetramethyl acetal at 60 °C. for 8 hours. The fiber thus obtained showed a weight increase due to acetalization of the fiber corresponding to 12.1% of the hydroxyl groups in the polyvinyl alcohol. The knot strength was 1.15 g./d. and the knot elongation was 10.1%.

We claim:
1. A process for improving the knot strength and elastic recovery of polyvinyl alcohol fibers which consists essentially of rapidly acetalizing the said fibers by reaction with an aldehyde consisting essentially of an aliphatic dialdehyde selected from the group consisting of succinic dialdehyde and glutaric dialdehyde, in an aqueous solution containing a high concentration of a catalyst selected from the group consisting of sulfuric acid, phosphoric acid, and hydrochloric acid, the concentration of sulfuric acid in said aqueous solution being at least 8% by weight when sulfuric acid is employed, the concentration of hydrochloric acid in said solution being at least 2% by weight when hydrochloric acid is employed, and the concentration of phosphoric acid in said solution being at least 10% by weight when phosphoric acid is employed, the acetalization being carried out until the weight of the fibers is increased due to the acetalization by about 1 to 20%, said acetalization being carried out at a temperature of 40 to 70 °C.

2. A process for improving the knot strength and elastic recovery of polyvinyl alcohol fibers which consists essentially of rapidly acetalizing the said fibers by reaction with an aldehyde consisting essentially of an aliphatic dialdehyde selected from the group consisting of succinic dialdehyde and glutaric dialdehyde in an aqueous solution containing a high concentration of at least 8% by weight sulfuric acid catalyst until the weight of the fibers has increased due to the acetalization by about 1 to 20%, said acetalization being carried out at a temperature of 40 to 70 °C.

3. A process for improving the knot strength and elastic recovery of polyvinyl alcohol fibers which consists essentially of rapidly acetalizing the said fibers by reaction with an aldehyde consisting essentially of an aliphatic dialdehyde selected from the group consisting of succinic dialdehyde and glutaric dialdehyde in an aqueous solution containing a high concentration of at least 2% by weight hydrochloric acid catalyst until the weight of the fibers has increased due to the acetalization by about 1 to 20%, said acetalization being carried out at a temperature of 40 to 70 °C.

4. A process for improving the knot strength and elastic recovery of polyvinyl alcohol fibers which consists essentially of rapidly acetalizing the said fibers by reaction with an aldehyde consisting essentially of an aliphatic dialdehyde selected from the group consisting of succinic dialdehyde and glutaric dialdehyde in an aqueous solution containing a high concentration of at least 10% phosphoric acid catalyst until the weight of the fibers has increased due to the acetalization by about 1 to 20%, said acetalization being carried out at a temperature of 40 to 70 °C.

5. The method of claim 1 wherein the aliphatic dialdehyde is glutaric dialdehyde.

6. The method of claim 1 wherein the aliphatic dialdehyde is succinic dialdehyde.

7. A process for improving the knot strength and elastic recovery of polyvinyl alcohol fibers as defined in claim 1, wherein said fibers are heat treated prior to acetalization.

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