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PROCESS FOR IMPROVING THE STRENGTH OF WOOL OR SILK FIBERS AND PRODUCTS THEREOF

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ABSTRACT OF THE DISCLOSURE

The tensile strength of wool and silk fibers can be increased by treating such fibers with an aqueous dispersion of a dialdehyde polysaccharide.

This invention relates to proteinaceous natural fibers having improved tensile strength. More particularly, it relates to wool or silk fibers which have been treated with an aqueous dispersion of a dialdehyde polysaccharide, said treated fibers having improved tensile strength as compared to untreated fibers.

Natural proteinaceous fibers, and especially wool and silk fibers, are widely used in the textile industry. Wool, for example, is valued for the warmth, resilience and crease and crush resistance of its fabrics. Its average tensile strength, however, is quite low and wool fabrics are therefore easily deteriorated when subjected to localized physical force. Wool is also subject to attack by bacterial action or by chemicals, such as acids, which weaken its strength. Silk is known to have a natural tensile strength higher than that of wool, but it is still desired to improve the strength of silk so as to be more competitive with synthetic fibers of high strength.

It is an object of the present invention to provide natural proteinaceous fibers having improved tensile strength.

It is another object of the present invention to provide natural proteinaceous fibers which are more resistant to attack by bacterial action or by chemical action.

It is a further object to provide a process for treating natural proteinaceous fibers to improve their tensile strength.

In accordance with the present invention a process is provided which comprises contacting a natural proteinaceous fiber, such as wool or silk, with an aqueous dispersion of a dialdehyde polysaccharide and forming a fiber-dialdehyde polysaccharide raection product. The concentration of the dialdehyde polysaccharide in the aqueous dispersions useful in the present invention is from about 0.1 to about 10 weight percent based on the total weight of the dialdehyde polysaccharide and water. Preferably, the concentration is from about 0.15 to about 5 weight percent.

These dispersions can be prepared by cooking the dialdehyde polysaccharide in water to rupture the granules of the dialdehyde polysaccharide. The cook is generally considered to be complete when no unruptered granules are found to be present. This can be ascertained, if desired, by means of centrifugation or by other appropriate analytical means. Sometimes the dispersion of the dialdehyde polysaccharide can be facilitated by the use of a small amount of a buffer salt, such as sodium acetate, sodium citrate, monosodium phosphate, borax or sodium hexametaphosphate. In general, the amount of buffer salt used should be in the range of from about 0.1 to about 5 weight percent based on the weight of the dialdehyde polysaccharide used. The dispersion temperature is generally from about 60° C. to about 95° C.

Following the step of dispersing the dialdehyde polysaccharide in water, the pH of the resulting dispersion, if not already in the range of from about 2 to about 7, is adjusted to a value within this range by the addition of a suitable reagent, such as sulfuric acid to lower the pH or sodium hydroxide to increase the pH. A dispersion pH within this range prevents alkaline degradation of the dialdehyde polysaccharide and provides an improved reaction bond between the dialdehyde polysaccharide and the wool or silk fibers.

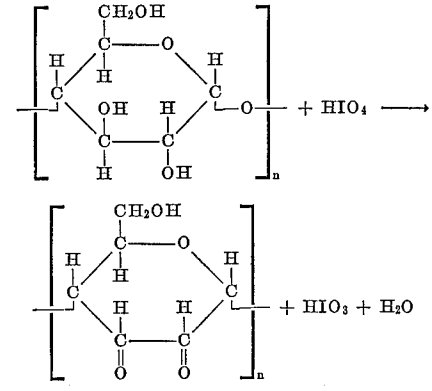
Following adjustment of the pH of the aqueous dialdehyde polysaccharide dispersion, such dispersion is then brought into contact with the wool or silk fibers to provide a reaction therebetween. Such reaction takes place at a temperature from about 20° C. to about 40° C. for from about 5 minutes to about 60 minutes.

After treatment with the aqueous dialdehyde polysaccharide dispersion, the wool or silk fibers are then washed with water at room temperature (about 20° C.–25° C.) and then dried at room temperature. The resulting fibers can then be employed in the production of textiles having improved strength.

The present invention also has other advantages. Wool is subject to deterioration caused by physical force, bacterial action or chemical action. If partially deteriorated wool is treated with an aqueous dispersion of dialdehyde polysaccharide according to the present invention some of the fiber strength can be restored.

It has also been found that wool treated in accordance with the present novel process has improved resistance to deterioration by bacterial or chemical action.

The dialdehyde polysaccharides utilized in the process of this invention are well known in the art. Such materials are frequently referred to as periodate oxidized polysaccharides because of their preparation by the well known oxidation of polysaccharides with periodic acid. This preparation can be illustrated by the conversion of a polysaccharide, such as starch, to dialdehyde starch or periodate oxidized starch using periodic acid in accordance with the following equation:



wherein *n* stands for the number of repeating structural units in the molecule, which may range from as few as about 20 to as many as several thousand. The preparation of dialdehyde starch is more particularly described in U.S. Patent Nos. 2,648,629 of W. Dvonch et al. and 2,713,553 of C. L. Mehltretter.

The dialdehyde polysaccharides to be used in preparing the novel reaction products of the present invention may be the dialdehyde derivatives of any polysaccharide, such as corn, wheat, rice, tapioca or potato starches, amyloses, amylopectins, celluloses, gums, dextrans, algins, inulins and the like. Of these polysaccharides, the dialdehyde derivatives of starch, known generically as dialdehyde starch, are the best known and most widely used. However, where it is desired to have dialdehydes of other polysaccharides, these may be used as well. The dialde-

hyde polysaccharides useful in the present invention can contain from about 0.5 to about 100 mole percent dialdehyde polysaccharide units. In general, it is preferred to use dialdehyde polysaccharides which are about 90 to 100 percent oxidized, i.e., those wherein about 90 to 100 out of each 100 of the original anhydroglucose units have been converted to dialdehyde units such as by periodate oxidation as above described.

It is not known exactly how the dialdehyde polysaccharide reacts with the wool or silk fibers so as to increase the fiber tensile strength. Natural proteinaceous fibers, such as wool or silk, are formed from polypeptide chains containing reactive groups such as free amino groups and free —SH groups in such chains. The dialdehyde polysaccharide can possibly react with such groups to form cross-linking bonds between such reactive groups of adjacent polypeptide chains and thus increase the internal strength of each of the fibers which are composed of multiple polypeptide chains.

It can be readily shown that the dialdehyde polysaccharide is retained on the wool or silk fibers after reacting therewith. Even though some of the carbonyl groups of the dialdehyde polysaccharide react with the fibers, there are still some unreacted aldehyde groups remaining These unreacted aldehyde groups within the fibrous polymer chain are available to undergo well known reactions with aldehyde reagents. Colored dye staining reagents, such as the sulfurous acid solution of the disodium salt of the trisulfonic acid of rosaniline (Fuchsin solution) have been found extremely useful in qualitatively determining the presence of the dialdehyde polysaccharide. If an untreated wool or silk fiber is contacted with the Fuchsin solution, a bright red color is developed after about 20 minutes. In contrast to this, a wool or silk fiber treated with a dialdehyde polysaccharide develops a deep blue-reddish color within only about 1–5 minutes after contacting Fuchsin solution. This fast color development is due to reaction between free aldehyde groups of the dialdehyde polysaccharide retained by the fiber and the Fuchsin solution.

The invention will be further described in the following examples.

EXAMPLE 1

A 176 g. quantity of dialdehyde corn starch being about 95 percent oxidized was added to an aqueous solution of 4.4 g. borax and 1600 ml. of distilled water at 65° C. The mixture was mechanically stirred for 55 minutes while maintaining the mixture temperature at 65° C.–70° C. During this time the dialdehyde corn starch was substantially completely dispersed. A 0.1 g. quantity of a siliceous filter aid was added to the dispersion and the mixture was filtered warm through a vacuum filter. The filtrate was an aqueous dispersion of 10 weight percent dialdehyde starch. It was then cooled to room temperature and divided into three portions. Such portions were then diluted with appropriate quantities of distilled water to form dispersions having dialdehyde starch concentrations of 0.25 weight percent, 0.5 weight percent, and 1.0 weight percent, respectively.

Three strands of defatted sheep wool were soaked for two hours at room temperature (about 20° C.–25° C.) in distilled water containing 6 drops/liter of an anionic surfactant. This surfactant is marketed under the trade name of Tergitol Anionic 4 by Union Carbide Chemicals Co. The three strands were then washed three times with water and then treated as follows:

Strand (1) was soaked for 30 minutes at 25° C. in an aqueous dispersion containing 0.5 weight percent dialdehyde starch having a pH of 5.8.

Strand (2) was soaked for 30 minutes at 25° C. in an aqueous dispersion containing 1.0 weight percent dialdehyde starch having a pH of 5.8.

Strand (3) was soaked for 30 minutes at 25° C. in distilled water having a pH adjusted to 5.8.

All the strands were then removed from the solutions, washed twice with distilled water and then heated to 100° C. for 3 minutes. The strands were washed again with distilled water and then wiped dry with a towel. Further drying was carried out at room temperature for 5 hours. Between 10–12 single fibers were then isolated from each strand and were tested for tensile strength using commonly available testing apparatus.

The following tests results were obtained:

TABLE 1

Treating Solution	Average Tensile Strength (lbs.)	Tensile Strength Increase Over Control, percent
Water (Control)	0.361	
0.5% dialdehyde starch	0.425	173.
1.0% dialdehyde starch	0.402	11.7

It can be readily seen from the above data that treating a natural proteinaceous fiber, such as wool, with an aqueous dispersion of a dialdehyde starch remarkably increases the tensile strength of the treated fiber. It was also found that the treated fibers were more resistant to deterioration from bacterial action and chemical action the untreated fibers.

EXAMPLE 2

An aqueous dispersion containing 0.25 weight percent dialdehyde starch, prepared as described in Example 1, was divided into four portions. The pH values of these four portions were adjusted to 3.6, 5.1, 6.7 and 7.4, respectively. Four strands of defatted sheep wool, each weighing 1 g., were separately soaked in 200 ml. portions of the above aqueous dispersions for 30 minutes at 25° C. A fifth strand of sheep wool was soaked in distilled water for 30 minutes at 25° C. and pH 6.2. The strands were then removed from the solutions, washed twice with distilled water and allowed to dry at room temperature for 5 hours. Individual fibers from each strand were then tested for tensile strength.

Fibers from each strand were also subjected to a "Fuchsin Test." A 0.5 g. quantity of Fuchsin acid (disodium salt of the trisulfonic acid of rosaniline) was dissolved in 500 ml. of distilled water at 60° C. The deep reddish solution was decolorized by saturating the solution with sulfur dioxide. A second solution consisting of 50 weight percent dilute sulfurous acid was also prepared. Before use a mixture was prepared consisting of 3 parts by volume Fuchsin solution and 1 part by volume of the sulfurous acid solution. The fiber to be tested was dipped in such mixture for 3–20 minutes. Wool fiber treated with dispersions of dialdehyde starch generally develops a deep-blue-reddish color within 3–10 minutes, while untreated fiber develops a red color after about 20 minutes.

The test results are shown below:

TABLE 2

Treating Solution (Wt. percent dialdehyde starch)	Treating Solution, pH	Average Tensile Strength (lbs.)	Tensile Increase Over Control, percent	Fuchsin Test
0	6.2	0.310		Red color after 20 min.
0.25	3.6	0.435	40.3	Blue-red color in 3–5 min.
0.25	5.1	0.347	11.9	Blue-red color in 10 min.
0.25	6.7	0.445	43.6	Blue-red color in 3–5 min.
0.25	7.4	0.307		Red color in 20 min.

It can be seen from the the above data that aqueous dispersions of dialdehyde starch having pH values in the range from 2 to 7 can be employed to react with wool fibers to increase the tensile strength of the wool fibers. It can also be seen that the dialdehyde starch is retained on the treated fibers as indicated by the Fuchsin Test.

While the above disclosure is directed primarily at treating wool with dialdehyde corn starch, it should be understood that silk and other dialdehyde polysaccharides can be employed in accordance with the present invention.

In summary, the present invention involves treating wool or silk fibers with an aqueous dispersion of a dialdehyde polysaccharide, such as dialdehyde starch, at a pH of from about 2 to about 7 to cause a reaction between the wool or silk fibers and the dialdehyde starch so as to increase the tensile strength of the fibers.

What is claimed is:

1. A process for improving the strength of wool or silk fibers which comprises contacting the wool or silk fibers for from about 5 minutes to about 60 minutes at a temperature from about 20° C. to about 40° C. with an aqueous dispersion of a dialdehyde polysaccharide, said dispersion containing from about 0.1 to about 10 weight percent dialdehyde polysaccharide and having a pH value of from about 2 to about 7.

2. A process according to claim **1** wherein the dialdehyde polysaccharide is dialdehyde starch.

3. A process according to claim **1** wherein the fiber is wool.

4. A process according to claim **1** wherein the fiber is silk.

5. A process according to claim **1** wherein the aqueous dispersion of dialdehyde polysaccharide contains from about 0.15 to about 5 weight percent of a dialdehyde polysaccharide.

6. A fiber material having improved tensile strength consisting essentially of wool or silk fibers treated in accordance with the process of claim **1.**

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