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METHOD OF PRODUCING VINYL ALCOHOL POLYMER FIBERS AND PRODUCTS THEREOF

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The invention relates to the manufacture of water-soluble filaments, fibers, yarns, threads and the like.

It is known that polyvinyl alcohol fibers as obtained by spinning without after-treatment, are more or less water soluble. However, they have not sufficient strength to be useful for textile purposes and other industrial applications.

It is a principal object of the invention to provide a fiber on polyvinyl alcohol basis, which is useful as a textile fiber.

It is another object of the invention to provide a method for preparing water soluble fibers on polyvinyl alcohol basis which have increased mechanical strength.

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

According to the invention, fibers which are soluble in water of 50° C. and below and have the strength required for textile manipulations are obtained from conjoint polymers of vinyl alcohol and allyl alcohol. Such copolymers are best obtained by the saponification of the copolymers of organic vinyl esters with allyl esters or allyl alcohol. Suitable esters are the esters of lower aliphatic acids, particularly of acetic acid, but the esters of formic acid, propionic acid, butyric acid and the like may also be used. Such conjoint esters are readily prepared and saponified by conventional procedures. The obtained polyvinyl alcohol-allyl alcohol copolymer dissolves in cold water and can be spun by the usual wet and dry spinning methods. In wet spinning, concentrated solutions with above two thirds of the saturated solubility of the coagulating salts, such as sodium sulphate or ammonium sulphate, must be used. The cold water solubility of the obtained fibers is even retained when the fibers are heated for a short period of time at high temperatures in air or other gases which do not attack the copolymer, in order to improve their mechanical properties.

The water solubility of the fibers increases with increasing allyl alcohol content. This is shown by the following tests made with fibers of the same polymerization degree. The dissolving temperature was determined by placing the fiber in water of 0° C. and raising the temperature of the water by 1° C. per minute.

Mol percent Allyl Alcohol	0	0.5	0.9	1.8	2.2	2.6	3	3.5	4.4
Dissolving Temp., ° C.	70	67	61	54	30	23	20	17	14
Tenacity, g./d.	3.4	3.3	2.5	2.0	3.0	3.0	2.0	2.5	2.9

The table shows that in order to be soluble in water of 50° C. and below, the fibers must contain an allyl alcohol content of at least about 2 mole percent. The upper limit is about 10 mol percent, as with higher proportions of allyl alcohol the tenacity of the fibers decreases to such an extent that the fibers are no longer suitable for textile purposes. Generally, the optimum content will be about 2.5 to 5 mol percent of allyl alcohol.

In wet spinning, a high allyl alcohol content of the conjoint polymer may affect the speedy coagulation in a conventional spinning bath. A preferred embodiment of the invention consists, therefore, in spinning together mixtures of the vinyl alcohol-allyl alcohol polymer with vinyl alcohol homopolymer. The allyl alcohol content of the obtained fibers can readily be adjusted to the desired degree by adjusting the ratio of copolymer to homopolymer as a function of the allyl alcohol content of the copolymer. In this case, the intrinsic viscosity (conc.=g./l.) of the solution must be used above 0.025 at 30° C., and so in the following equation:

$$[\eta]=8.33\times10^{-4}P^{0.62}$$

the required minimum DP of the copolymer and its mixture with the homopolymer must be used above 250. Also, fibers prepared from such mixtures have the required tenacity and water solubility.

The novel fibers are useful for specialty sewing threads, alone or together with other fibers to obtain in woven material effects which cannot be produced by other means. Twisted with cotton or nylon fibers, a sewing thread can be made which will shrink to a predetermined degree and prevent the obnoxious puckering of seams. When the novel fibers are twisted with a fully synthetic thermoplastic fiber, such as nylon, Dacron, and the like, a permanent twist can be applied to said thermoplastic fibers by first setting the twist and then washing out the polyvinyl alcohol-allyl alcohol fiber, thereby producing a permanently elastic fiber. Fabrics produced from the novel fiber are, for instance, useful for the manufacture of water soluble parachutes. As will be seen from the foregoing, the novel fiber opens up a vast field of new applications; for instance, in the manufacture of filter cloth, lace, knitted fabrics, and the like, effects can be obtained which cannot be produced by other means.

The following specific examples are given to illustrate the invention but they are not intended to limit it thereto; the parts are by weight.

Example 1

291 parts of vinyl acetate and 9 parts of allyl acetate were mixed and polymerized in the presence of 0.6 part of benzoyl peroxide. After an about 50% polymerization was obtained, 100 parts of methanol were slowly added, and the polymerization was continued until after 20 hours, a polymer yield of 90% was obtained. The copolymer was freed from unreacted monomers, dissolved in methanol and cold saponified by adding a methanol solution of caustic soda to the methanol solution of the polymer. The polyvinyl alcohol-vinyl alcohol copolymer was obtained as a white powder containing 3 mol percent of allyl alcohol and having a DP of 1160. The copolymer was dissolved in water to a 13% solution, which was spun into a saturated solution of Glauber salt. The obtained white fibers had a tenacity of 3.3 g./d. and dissolved instantaneously in water of 23° C.

Example 2

A vinyl alcohol-allyl alcohol copolymer was prepared according to the procedure set forth in Example 1. It contained 4.4 mol percent of allyl alcohol, had an average DP of 700, and was soluble in water at 14° C. 60 parts of said copolymer were mixed with 40 parts of vinyl alcohol homopolymer having an average DP of 1630 and a saponification degree of 99.8°, which was soluble in water at 70° C. The mixture was dissolved in water to a 15% solution, using the method described in Patent No. 2,642,333. The obtained fiber had, after drying, a tenacity of 3.0 g./d. and was soluble in water at 30° C.

Example 3

A 6% aqueous solution of a vinyl alcohol allyl-alcohol copolymer containing 3 mol percent of allyl alcohol and having an average DP of 930 was spun to filaments by extruding the solution through a spinneret into a column of hot air of 110–120° C. The solidified filaments had a tenacity of 1.5 g./d. and were soluble in water at 22° C.

As various embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. A fiber soluble in water at 50° C. and having a tenacity of at least about 1.5 g./d. comprising a vinyl alcohol-allyl alcohol copolymer containing 2 to 10 mol percent of allyl alcohol.

2. A fiber soluble in water at 50° C. and having a tenacity of at least about 1.5 g./d. consisting essentially of a mixture of a vinyl alcohol-allyl alcohol copolymer

with vinyl alcohol homopolymer and containing 2 to 10 mol percent of allyl alcohol.

3. A method of producing synthetic fibers which have a tenacity of at least about 1.5 g./d. and are soluble in water of 50° C., said method comprising mixing a vinyl alcohol-allyl alcohol copolymer and a vinyl alcohol homopolymer in such proportions that the combined polymers contain 2 to 10 mol percent of allyl alcohol, dissolving said mixture in water and extruding said solution through a spinneret into a substantially saturated coagulating solution.

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