United States Patent

Kawai et al.

[15] **3,697,637**

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[54] **METHOD FOR PRODUCING HIGHLY CRIMPED REGENERATED CELLULOSE FIBERS BY STEAM STRETCHING**

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[51] **Int. Cl.**.....**D01f 3/28**

[58] **Field of Search**.....264/188–198, 168, 264/343; 8/131

[56] **References Cited**

UNITED STATES PATENTS

2,317,152	4/1943	Costa et al.	264/196
3,109,699	11/1963	Richardson	264/198
3,419,652	12/1968	Kubota et al.	264/168
3,494,995	2/1970	Thomas et al.	264/188
3,574,812	4/1971	Kubota et al.	264/197

Primary Examiner—Jay H. Woo
Attorney—Fisher, Christen and Sabol

[57] **ABSTRACT**

Highly crimped regenerated fibers can be obtained by stretching filaments containing the reaction product of cellulose xanthate and formaldehyde in a humidified atmosphere having a relative humidity of more than 50 % and kept at a temperature of 40° to 130° C., relaxing said filaments while in a state of regeneration degree of less than 89 % in a liquid having a swelling action on said filaments and maintained at a temperature of 30° to 90° C. and then subjecting the filaments to regeneration treatment to complete regeneration.

12 Claims, 2 Drawing Figures

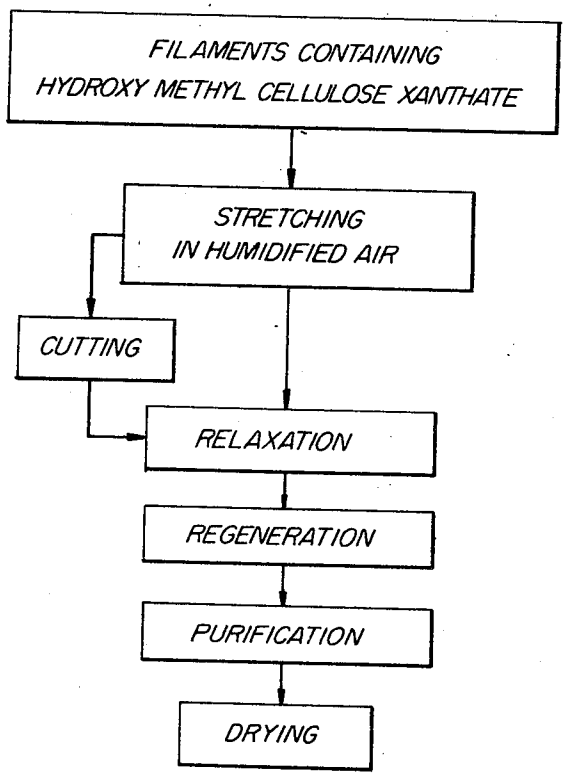


FIG. 1

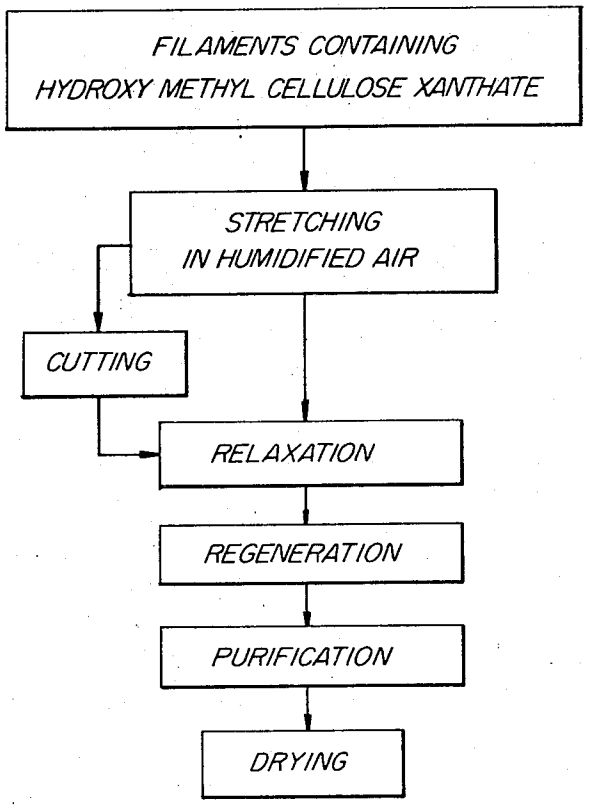
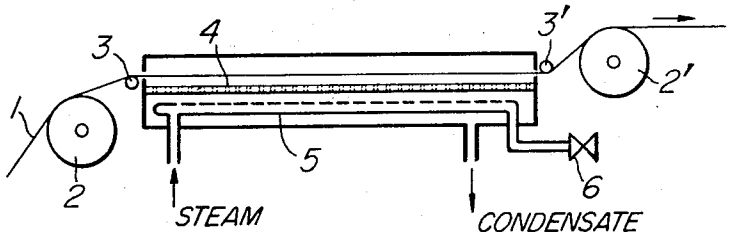

FILAMENTS CONTAINING
HYDROXY METHYL CELLULOSE XANTHATE
STRETCHING
IN HUMIDIFIED AIR
CUTTING
RELAXATION
REGENERATION
PURIFICATION
DRYING

FIG. 2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CONDENSATE

METHOD FOR PRODUCING HIGHLY CRIMPED REGENERATED CELLULOSE FIBERS BY STEAM STRETCHING

This invention relates to a novel method for producing highly crimped regenerated cellulose fibers by the viscose method.

The object of this invention is to produce highly crimped regenerated cellulose fibers having water reversible micro crimps and possessing excellent fiber properties and spinnability for preparing fine count yarn. Furthermore, fabrics made from said fibers have excellent hand and bulk as compared with those from conventional ordinary rayon, polynosic fibers, high wet modulus rayon, etc. Methods for producing highly crimped regenerated cellulose fibers from which fabrics of excellent hand can be obtained were earlier proposed in U.S. Pat. Nos. 3,419,652 and 3,574,812 . However, fibers obtained by these methods are difficultly spun to fine count yarn. This invention resides in overcoming said problems and can produce fibers having excellent spinnability and fiber properties. The fibers obtained according to this invention are characterized by three dimensional microcrimps, more than 40 crimps per inch, and they have excellent spinnability and fiber properties.

The method of this invention comprises stretching filaments containing the reaction product of cellulose xanthate and formaldehyde in a humidified atmosphere having a relative humidity of more than 50 % and kept at a temperature of 40° to 130° C, relaxing said filaments while in a state of regeneration degree of less than 89 % in a liquid which has a swelling action on said filaments and is maintained at a temperature of 30° to 90° C and then subjecting the filaments to regeneration treatment to complete the regeneration.

The characteristic of this invention resides in the combination of novel stretching conditions and relaxation conditions, but said stretching conditions are more important. That is, in the method proposed U.S. Pat. Nos. 3,419,652 and 3,574,812, filaments containing the reaction product of cellulose xanthate and formaldehyde are stretched in an acidic aqueous solution under a tension of less than 0.3 g/d in order to form a non-symmetrical heterogeneous structure in cross section similar to conjugate fibers and then the thus stretched filaments are relaxed in a bath having a swelling action on the filaments in a state of incomplete regeneration. On the other hand, according to this invention, the filaments are stretched in a humidified atmosphere and the stretched filaments are swollen in an incompletely regenerated state, namely at a regeneration degree of less than 89 %, to relax them.

As mentioned above, the first point of the method of this invention is to produce the reaction product of formaldehyde and cellulose xanthate as filaments, the second point is to stretch the thus obtained filaments in humidified atmosphere to form a heterogeneous structure in cross section similar to conjugate fibers and the third point is to relax the stretched filaments which still contain the reaction product in a bath having a swelling action on said filaments to develop the heterogeneous structure formed in the stretching step.

The reaction between formaldehyde and cellulose xanthate takes place in accordance with the following equation (I) and proceeds in an acidic medium. cell—$O—CS_2^- + {}^+CH_2OH \rightleftharpoons$ cell—$O—CS_2—CH_2OH$ (1)

The amounts of xanthate and formaldehyde and acid concentration of the system affect said reaction. Accordingly, the cellulose xanthate ion is unstable in an acidic state, but the formaldehyde derivative of cellulose xanthate is relatively stable in an acidic state. However, in an aqueous solution, hydrolysis as shown in the following equation (2) takes place even in an acidic state, so that the decomposition rate increases with an increase in temperature. In an aqueous solution, the decomposition rate abruptly increases when the temperature exceeds 55° to 60° C.

$$\text{cell—O—CS}_2\text{—CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{cell—OH—CS}_2 + \text{HOCH}_2\text{OH} \quad (2)$$

On the other hand, in a non-aqueous medium, the formaldehyde derivative of cellulose xanthate is very stable even at high temperatures.

The heterogeneous fiber structure in cross section which is similar to that of conjugate fibers is formed in the stretching step. In order to attain effective stretching, it is necessary to increase mobility of the formaldehyde derivative molecules and to provide deviation in distribution of the molecules in the filaments. For this purpose, it is effective to change the fiber structure in a short period of time, namely, to stretch the filaments in a medium at a high temperature. However, as mentioned above, in an aqueous solution, decomposition of the formaldehyde derivative takes place at high temperatures, whereby formation of a heterogeneous structure is prevented and thus development of crimps is suppressed. According to this invention, these drawbacks are overcome since a humidified atmosphere is used as the stretching medium. The difference between the method of this invention which uses a humidified atmosphere as the stretching medium and the conventional method which uses an aqueous solution as the stretching medium resides in the heat transfer and material transfer between the filaments and stretching medium.

In the conventional aqueous solution, since (a) diffusion of water and acid into filaments is rapid in an acidic aqueous solution at high temperatures, (b) the formaldehyde derivative is easily decomposed with water at high temperatures, (c) the remaining cellulose xanthate ion is also easily decomposed with acid at high temperatures and (d) the fiber structure is fixed by decomposition of the formaldehyde derivative and the remaining cellulose xanthate ion, development of the heterogeneous structure is prevented. In this invention, little material transfer to the outside of the system takes place during stretching and a high degree of stretch is possible at high temperatures.

Therefore, according to this invention, development of the heterogeneous structure is easier than according to the methods of U.S. Pat. Nos. 3,419,652 and 3,574,812. In the methods of U.S. Pat. Nos. 3,419,652 and 3,574,812, in order to obtain crimps, the stretching is carried out in an aqueous solution under a stretching tension of less than 0.3 g/d, while according to this invention, stretching may be carried out under a wide tension range to develop a heterogeneous structure. Therefore, this invention provides great improvement of fiber properties, especially tenacity, wet modulus and spinnability as compared with the method of U.S. Pat. Nos. 3,419,652 and 3,574,812. Furthermore, according to this invention, processability and producibility are improved.

In the accompanying drawings FIG. 1 is a block diagram illustrating the general aspects of the process of this invention and FIG. 2 shows one example of a stretching apparatus for carrying out the method of this invention.

This invention will be explained in more detail hereinbelow.

The first point of this invention is to form the reaction product of formaldehyde and cellulose xanthate (which mainly consists of hydroxymethyl cellulose xanthate) in filament form and for this purpose, various means may be employed. For example, filaments containing hydroxymethyl cellulose xanthate may be produced by extruding viscose to which formaldehyde is added or by adding formaldehyde to a coagulation bath or by treating coagulated filaments containing cellulose xanthate with an aqueous solution of formaldehyde.

Viscose used in this invention preferably contains 2 to 8 percent total alkali. The viscose when spun must have a salt point of at least 16, preferably of 18 to 23. When formaldehyde is added to viscose, the amount of the former is preferably 0.2 to 2 percent based on the weight of viscose.

The coagulation bath contains preferably 20 to 250 g/l sodium sulfate, less than 0.3 g/l zinc sulfate and sulfuric acid in an amount within the range shown by the following equations:

Minimum concentration of sulfuric acid (g/l) = 3A + 8

Maximum concentration of sulfuric acid (g/l) = 8A + 16 wherein A is total alkali concentration (%) in the viscose. When formaldehyde is not added to the viscose, the coagulation bath contains preferably 4 to 20 g/l formaldehyde. When formaldehyde is added to the viscose, the formaldehyde concentration in the coagulation bath may be 1 to 6 g/l. The temperature of the coagulation bath is lower than 45° C, desirably 10° to 35° C.

Filaments containing hydroxymethyl cellulose xanthate may also be obtained by extruding viscose into a coagulation bath containing 14 to 50 g/l sulfuric acid, 20 to 250 g/l sodium sulfate and less than 1 g/l zinc sulfate at a temperature of lower than 35° C and treating thus coagulated filaments with an aqueous solution containing 15 to 70 g/l formaldehyde without adding formaldehyde to the viscose or the coagulation bath.

In all the above cases, the coagulation bath or the viscose may contain various surface active agents.

The second point of this invention resides in the step of stretching the filaments containing hydroxymethyl cellulose xanthate to form the heterogeneous structure. In this invention, a humidified atmosphere is used as the stretching medium because the humidified atmosphere contains a great amount of latent heat. The water content in the humidified atmosphere used is preferably more than 50 % calculated as relative humidity and saturated steam is most preferred atmosphere.

Regarding the stretching apparatus, for example, a steam stretch box as shown in FIG. 2 may be used. In FIG. 2, 1 is filaments, 2 and 2′ are godet rollers, 3 and 3′ are guides, 4 is a perforated plate, 5 is a perforated steam pipe, 6 is a trap and 7 is holes. Filaments 1 are passed through the space above the perforated plate 4, during which the filaments are stretched. The temperature of humidified atmosphere should be higher than 40° C and lower than 130° C. If the temperature is below 40° C, mobility of hydroxymethyl cellulose xanthate is low, the stretchability is decreased and formation of the heterogeneous structure is insufficient. In principle, a higher temperature is desirable, but decomposition of hydroxymethyl cellulose xanthate is also accelerated at high temperatures, and development of crimps is reduced when the regeneration degree of filaments introduced into the relaxation bath after stretching becomes too high. Thus, it is necessary to control the stretch temperature and residence time in the heating medium. When the temperature exceeds 130° C, even treatment for a short time caused adverse results. The preferred stretch temperature is 80° to 100° C.

Furthermore, it is necessary to prevent drops of condensed water in the stretching box from contacting the filaments. When drops of water at high temperatures contact the filaments, regeneration of the portion of the filaments contacted by the water progresses and results in prevention of development of crimps.

Stretching in a humidified atmosphere may be effectively carried out on a heated body such as heated rollers and in this case the temperature of humidified atmosphere may be relatively low.

The stretch ratio is also important for formation of heterogeneous structure.

The suitable stretch ratio for attaining the object of this invention is generally from 0.25 to 0.8 times the maximum stretch ratio at given conditions such as content of hydroxymethyl cellulose xanthate, temperature of the stretching medium etc. The maximum stretch ratio is defined as follows: The stretch tension increases with an increase in stretch ratio, but when the stretch ratio exceeds a certain value, filaments begin to break. With an increase in number of broken filaments, the stretch tension decreases. The stretch ratio which provides said maximum stretch tension is defined as the maximum stretch ratio (%). (Stretching to 2 times is 100 % and to 3 times is 200 %). When the stretch ratio is less than 0.25 times or more than 0.8 times the maximum stretch ratio, formation of the heterogeneous structure is insufficient.

The filaments stretched in the humidified atmosphere should then be subjected to a relaxation treatment in a relaxation bath while having a regeneration degree of less than 89 %. The un-regenerated portion of the filaments after stretching mainly comprises hydroxymethyl cellulose xanthate, but when the regeneration degree is more than 90 % and the content of hydroxymethyl cellulose xanthate is small, the effects of the relaxation treatment are not achieved and crimps are not developed. Thus, in order to obtain the effects of relaxation, the filaments should still be in a thermodynamically active state. The term "regeneration degree" used herein designates a value represented by the ratio of the γ-value when the regeneration degree of viscose when spun is taken as 0 % and that of completely regenerated cellulose is 100 %. Thus, for example, when the γ-value of viscose when spun is 80 % and that of the filaments entering the relaxation bath after stretching is 32, the regeneration degree of the filaments is 60 % in accordance with

$$\frac{80-32}{80}\times 100(\%)$$

The regeneration degree of filaments entering the relaxation bath after stretching is preferably 20 to 80 %, within which range development of crimps is particularly satisfactory.

The third point of this invention is that said stretched filaments containing hydroxymethyl cellulose xanthate are relaxed to develop the heterogeneous structure formed during stretching. The relaxation medium and its temperature are important as relaxation conditions. The following three kinds of relaxation baths are preferably used as a medium having a swelling action on the filaments.

1. An aqueous solution at 30° to 90° C.

As said aqueous solution, water or water containing a small amount of an acid may be used and it may further contain surface active agents or other agents. The pH of the aqueous solution is preferably 2.0 to 10.5. If the pH is less than 2.0, swelling of hydroxymethyl cellulose xanthate and the development of crimps are not sufficient. On the other hand, if the pH is more than 10.5, the filaments are swelled to a great extent and begin to be dissolved. The pH is more preferably 3.0 to 8.0. **The temperature of the aqueous solution is particularly preferably** 40° to 80° C.

2 An aqueous solution containing inorganic salts or organic salts or mixtures thereof.

As said salts, alkali metal salts, alkaline earth metal salts or ammonium salts of inorganic or organic acids or mixtures thereof may be employed. Typical salts are sodium acetate, potassium tartarate, sodium sulfate, potassium thiocyanate, potassium hydrogen phosphate, magnesium chloride, sodium chloride, etc. In such aqueous salt solutions, swelling of the filaments containing hydroxymethyl cellulose xanthate is much greater and the effect of relaxation is greater than in an aqueous solution containing no salts. In such aqueous salt solutions, the effect of relaxation can be attained even at about a pH of 1.0, but the preferable pH value of the solution is 1.5 to 8.0. The concentration of the salts is preferably 1 to 100 g/l, particularly preferably 3 to 50 g/l. Salts of heavy metals such as zinc, cadmium, copper, nickel, cobalt, etc. tend to restrain swelling of the filaments. However, presence of a small amount of said heavy metal salts results in prevention of excess swelling of the filaments and is effective for obtaining fibers of balanced properties.

The concentration of said metal salts is less than 1 g/l, desirably less than 0.5 g/l.

The temperature of the solution is desirably 30° C to 90° C, especially 40° C to 80° C as with solution (1).

In the above solutions (1) and (2), formaldehyde may be present due to partial decomposition of hydroxymethyl cellulose xanthate. However, since formaldehyde tends to prevent swelling of the filaments, it is necessary to accelerate relaxation of the filaments by increasing the temperature of the relaxation bath as the concentration of formaldehyde increases in the bath.

(3) An organic solvent.

Typical organic solvents are nitrogen containing solvents such as formamide, dimethylformamide, dimethylacetamide, pyridine, acetonitrile, glutaronitrile, etc., cyclic ether compounds such as tetrahydrofurane, dioxane, etc., sulfur containing solvents such as dimethyl sulfoxide, diethyl sulfoxide, dimethylsulfone, ethylmethyl sulfone, etc., and water soluble ketones such as acetone, dioxyacetone, etc.lactones such as γ-butyrolactone, etc. In these media, filaments are dissolved or swollen. The above mentioned solvents may be used alone, or as a mixture or aqueous solution thereof. An aqueous solution of said organic solvents is preferred.

Filaments subjected to relaxation treatment as described above should then be subjected to a regeneration treatment because a considerable amount of hydroxymethyl cellulose xanthate still remains, although a portion of the hydroxymethyl cellulose xanthate is decomposed in the relaxation bath. The regeneration treatment may be carried out in an acidic aqueous solution at a high temperature or in a steam at a high temperature. The completely regenerated filaments are then scoured and dried by conventional methods. In this invention, crimps are developed during relaxation and further crimps, especially micro crimps, are additionally developed during drying. The crimps can be made latent by decrimping such as by imparting some tension to the filaments during the drying step or by stretching the crimped filaments after they are dried.

As explained above, the fibers obtained by the method of this invention have water reversible micro crimps, have excellent mechanical properties and further have a wet modulus which is markedly higher than ordinary crimped rayon. Therefore, fabrics made from fibers according to this invention have excellent strength and bulk, comfortable hand and high dimensional stability. Furthermore, since they have extremely excellent spinnability, spinning of fine count yarn is easy and they are suitable for blend spinning with synthetic fibers. Moreover, durable flame resistance can easily be imparted by blending, e.g. water insoluble organic phosphorus compounds into the viscose. Since the fibers of this invention have properties similar to those of high grade cotton, this invention can provide durable flame resistant fibers having cotton like properties.

Example 1

A viscose containing 8.0 % cellulose and 5.0 % alkali and having a viscosity of 170 poises, a salt point of 22 and a γ-value of 79 was extruded into a coagulation bath containing 40 g/l sulfuric acid, 90 g/l sodium sulfate and 12 g/l formaldehyde at 25° C. The filaments withdrawn from the coagulation bath were stretched to 320 % (maximum stretch ratio was 450) the original length of the filaments in a saturated steam atmosphere at 105° C. The stretched filaments were treated in a relaxation bath containing 0.2 g/l sulfuric acid, 10 g/l sodium sulfate and 0.1 g/l zinc sulfate at 50° C to develop crimps. The γ-value of the filaments just before entering the relaxation bath was 36, which was about 54 % expressed as regeneration degree.

Subsequently, regeneration of the filaments was completed in a bath containing 2 g/l sulfuric acid at 85° C.

Fiber properties of the thus obtained fibers (A) are shown in Table 1 and for comparison, those of fibers (B) produced in the same manner as above, except that the coagulated filaments were stretched to 175 % the original length in an aqueous solution containing 1 g/l sulfuric acid at 60° C are also shown in Table 1. When stretching was carried out in the aqueous solution at

60° C, the maximum stretch ratio was about 250 % and no crimps were developed at this value.

Table 1

Denier (d)	Conditioned tenacity (g/d)	Wet tenacity (g/d)	Conditioned elongation (%)	Wet elongation (%)
A 1.42	4.3	3.8	10.3	12.7
B 1.43	3.4	2.7	11.5	13.2

	Conditioned knot tenacity (g/d)	Number of crimps (per inch)	Wet modulus at 5 % elongation (g/d)
A	1.79	52	1.54
B	1.73	52	0.93

Example 2

A viscose containing 7.5 % cellulose and 4.5 % alkali and having a viscosity of 230 poises, a salt point of 22.5 and containing 0.05 % of a non-ionic surface active agent was extruded into a coagulation bath containing 33 g/l sulfuric acid, 90 g/l sodium sulfate, 0.05 g/l zinc sulfate and 10 g/l formaldehyde at 30° C. The coagulated filaments were stretched to 250 % (maximum stretch ratio was 390) the original length in saturated steam at 90° C and then were cut to staple lengths. The staple having a regeneration degree of 69 % were relaxed in an aqueous bath at pH of 6.5 and at 55° C. The staples were then regenerated in an aqueous bath containing 1 g/l sulfuric acid at 90° C and thereafter scoured and dried by conventional method (the thus obtained fibers are designated A in Table 2).

For comparison, fibers (B) were produced in the same manner as above, except that the filaments were stretched 150 % the original length in an aqueous solution containing 2 g/l sulfuric acid and 5 g/l sodium sulfate at 60° C.

Both fibers A and B were spun by a cotton system to obtain spun yarns having a cotton count of 45. The number of yarns breaking during the spinning of fibers A was 8/420 spindles/hr., while that of B was 17/420 spindles/hr. In Table 2, single fiber properties and yarn properties of fibers A and B are shown. Knitted fabrics made from both spun yarns had excellent bulk and firm hand which were similar to that of high grade cotton. On the other hand, knitted fabrics made from ordinary crimped rayon and commercially available polynosic fibers under the same conditions as above had a sleazy and limp hand.

TABLE 2

Mechanical properties of single fiber

Denier (d)	Conditioned tenacity (g/d)	Wet tenacity (g/d)	Conditioned elongation (%)	Wet elongation (%)	Number of crimps (per inch)
A 1.5	3.6	3.2	12	13	63
B 1.5	3.4	3.0	12	14	61

Properties of yarn

Yarn count (cc)	Conditioned tenacity (g)	Conditioned elongation (%)	Usters yarn eveness (U %)	Seriplane test yarn uneveness	Neps
A 45	220	6.5	11.8	185	195
B 45	190	6.2	13.4	173	180

Example 3

A viscose containing 7.5 % cellulose and 5.5 % alkali and having a viscosity of 210 poises, a salt point of 23 and a γ-value of 82 was prepared and deaired. Immediately before spinning, a 37 % aqueous solution of formaldehyde was added to the viscose so that 1.5 % formaldehyde was contained based on the weight of the viscose. This viscose was extruded into a coagulation bath containing 50 g/l sodium sulfate, 37 g/l sulfuric acid and 2g/l formaldehyde at 35° C.

The filaments withdrawn from the coagulation bath were stretched to 175% (maximum stretch ratio was 250) the original length in humidified air having a relative humidity (RH) of 55 % and being heated to a temperature of 60° C with a 250 W Infrared Heater, and thereafter were introduced into water at 60° C to relax and develop crimps. The γ-value of the filaments just before entering the relaxation bath was 41, which was about 50 % expressed as regeneration degree. Subsequently, regeneration of the filaments was completed in an aqueous solution containing 3 g/l sulfuric acid at 90° C.

Fiber properties of the thus obtained fibers A are shown in Table 3.

For comparison, properties of fibers (B) produced in the same manner as above, except that the filaments were stretched to 175 % the original length in an aqueous solution containing 1 g/l sulfuric acid at 65° C are also shown in Table 3.

TABLE 3

Denier (d)	Conditioned tenacity (g/d)	Wet tenacity (g/d)	Conditioned elongation (%)	Wet elongation (%)	Conditioned knot tenacity(g/d)
A 1.50	3.4	32	15	18	1.7
B 1.47	3.1	27	19	11	1.4

	Dye exhaustion (%)	Number of crimps (per inch)
A	54	73
B	42	38

Example 4

A viscose containing 7 % cellulose and 4 % alkali and having a viscosity of 190 poises, a salt point of 21 and a γ-value of 78 was prepared and was extruded into a coagulation bath containing 34 g/l sulfuric acid, 90 g/l sodium sulfate and 7 g/l formaldehyde at 25° C.

The coagulated filaments were passed at an average speed of 15 m/min through a Pyrex tube 2 cm. in diameter and 50 cm. in length which was provided with an external heater. The air temperature at the entrance of the tube was 85° C and the relative humidity of the air was 65 %. The filaments were stretched in said tube to 250 % (maximum stretch ratio was 320) the original length, were cut to staple length and then treated in a relaxation bath containing 0.2 g/l sulfuric acid, 10 g/l sodium sulfate and 0.1 g/l zinc sulfate at 55° C and sub-

sequently were subjected to regeneration treatment in a bath containing 2 g/l sulfuric acid at 85° C. The regeneration degree before relaxation was 65.

The properties of the fibers obtained are shown in Table 4.

TABLE 4

Denier (d)	Conditioned tenacity (g/d)	Wet tenacity (g/d)	Conditioned elongation (%)	Wet elongation (%)
1.52	3.5	3.3	15	17

Conditioned knot tenacity (g/d)	Dye exhaustion (%)	Number of crimps (per inch)
1.8	56	62

Example 5

A viscose containing 8.0 % cellulose and 5.5 % alkali and having a viscosity of 150 poises, a salt point of 21.5 and a γ-value of 80 was extruded into a coagulation bath containing 40 g/l sulfuric acid, 80 g/l sodium sulfate and 10 g/l formaldehyde at 25°° C.

The coagulated filaments were immediately led to a heated roller containing a heat source and upon which Teflon (polytetrafluoroethylene) was coated, wound around the roller, and then led to a second roller. The filaments were stretched to 250 % (maximum stretch ratio was 340) the original length between the heated roller and the second roller. The surface temperature of the heated roller was 102° C and relative humidity of the stretching atmosphere was 70 %. The regeneration degree before relaxation was 45 %. The stretched filaments were relaxed in an aqueous solution containing 2 % dimethylsulfoxide at 50° C to develop crimps and thereafter regenerated in an aqueous bath containing 2 g/l sulfuric acid at 85° C.

The properties of the fibers obtained are shown in Table 5.

TABLE 5

Denier (d)	Conditioned tenacity (g/d)	Wet tenacity (g/d)	Conditioned elongation (%)	Wet elongation (%)
3.0	3.7	2.9	12	14

Conditioned knot tenacity (g/d)	Dye exhaustion (%)	Number of crimps (per inch)
1.70	60	63

Example 6

A viscose containing 7.5 % cellulose and 4.5 % alkali and having a viscosity of 150 poises, a salt point of 22 and a γ-value of 80 was prepared. Thereafter, a 37 % aqueous solution of formaldehyde was added to said viscose so that it contained 2.0 % formaldehyde based on the weight of viscose immediately before spinning. This viscose was extruded into a coagulation bath containing 60 g/l sodium sulfate, 30 g/l sulfuric acid and 1 g/l formaldehyde at 35° C. The filaments withdrawn from the coagulation bath were stretched to 270 % (maximum stretch ratio was 405) the original length in saturated steam at 110° C and then were introduced into water at 70° C to develop crimps. The γ-value of the stretched filaments was 28, which corresponded to 65 % experssed as regeneration degree. Then, regeneration of the filaments was completed in an aqueous bath containing 2 g/l sulfuric acid at 85° C.

The properties of the obtained fibers A are shown in Table 6. For comparison, fibers B were produced in the same manner as above, except that the filaments were stretched to 150 % the original length in an aqueous solution containing 2 g/l sulfuric acid at 65° C and the properties of the thus obtained fibers B are also shown in Table 6. The conditions under which fibers B were produced were the optimum conditions of stretching in an aqueous medium.

TABLE 6

	Denier (d)	Conditioned tenacity (g/d)	Wet tenacity (g/d)	Conditioned elongation (%)	Wet elongation (%)
A	3.2	3.16	2.74	11.3	13.0
B	3.0	2.20	2.15	17.6	21.2

	Conditioned knot tenacity (g/d)	Number of crimps (per inch)
A	1.68	58
B	1.32	45

Example 7

A viscose containing 6.5 % cellulose and 4 % alkali and having a viscosity of 130 poises, a salt point of 20.5 and a γ-value of 76 was extruded into a coagulation bath containing 25 g/l sulfuric acid, 75 g/l sodium sulfate, 7 g/l formaldehyde and 0.1 g/l zinc sulfate. The filaments withdrawn from the coagulation bath were stretched to 220 % (maximum stretch ratio was 360) in super-saturated steam at 90° C and then relaxed in an aqueous solution containing 4 % dimethyl formamide at 55° C to develop crimps. The γ-value before entering the relaxation bath was 35, which corresponded to 54 % expressed as regeneration degree. Then, the filaments were subjected to regeneration treatment in an aqueous bath containing 2 g/l sulfuric acid at 85° C in the conventional manner.

The properties of the fibers thus obtained are shown in Table 7.

TABLE 7

Denier (d)	Conditioned tenacity (g/d)	Wet tenacity (g/d)	Conditioned elongation (%)	Wet elongation (%)
1.52	4.20	3.94	14.5	18.3

Conditioned knot tenacity (g/d)	Dye exhaustion (%)	Number of crimps (per inch)
1.76	62	70

Example 8

A viscose containing 7 % cellulose and 4.5 % alkali and having a viscosity of 250 poises and a salt point of 23 was extruded into a coagulation bath containing 30 g/l sulfuric acid and 60 g/l sodium sulfate at 20° C. The coagulated filaments were immediately passed through an aqueous solution containing 30 g/l formaldehyde and 10 g/l sulfuric acid at 25° C and then stretched to 180 % (maximum stretch ratio was 270) the original length in saturated steam at 80° C. The stretched filaments having a regeneration degree of 70 % were relaxed in an aqueous solution containing 30 % acetone at 35° C and then regenerated. The properties of the thus obtained fibers are shown in Table 8.

TABLE 8

Denier (d)	Conditioned tenacity (g/d)	Wet tenacity (g/d)	Conditioned elongation (%)	Wet elongation (%)
1.5	3.3	3.1	12	14

Conditioned knot tenacity (g/d)	Dye exhaustion (%)	Number of crimps (per inch)
1.9	68	59

What is claimed is:

1. A method for producing highly crimped regenerated cellulose fibers, which comprises stretching filaments containing the reaction product of cellulose xanthate and formaldehyde in a humidified atmosphere having a relative humidity of more than 50% and kept at a temperature of 40° to 130° C and at a stretch ratio of 0.25 to 0.8 times the maximum stretching ratio, relaxing said filaments while in a state of regeneration degree of less than 89% in a liquid having a swelling action on said filaments and maintained at a temperature of 30° to 90° C, said liquid being selected from the group consisting of:

a. an aqueous solution selected from water and water containing a small amount of an acid and maintained at a pH of 2.0 to 10.5;
b. an aqueous solution containing a member selected from inorganic and organic salts; and
c. a member selected from an organic solvent and an aqueous solution thereof,

and then subjecting the filaments to regeneration treatment to complete regeneration.

2. A method according to claim 1, wherein said humidified atmosphere is kept at a temperature of 80° to 100° C.

3. A method according to claim 1, wherein said stretching is carried out in saturated steam at a temperature higher than 80° C.

4. A method according to claim 1, wherein said relaxation is carried out in an aqueous solution maintained at a pH of 2.0 to 10.5.

5. A method according to claim 1, wherein said relaxation is carried out in an aqueous solution containing a member selected from inorganic and organic salts.

6. A method according to claim 1, wherein said relaxation is carried out in a member selected from an organic solvent and an aqueous solution thereof.

7. A method according to claim 5, wherein said salt is at least one compound selected from the group consisting of alkali metal salts, alkali earth metal salts and ammonium salts of inorganic and organic acids.

8. A method according to claim 6, wherein said organic solvent is at least one member selected from the group consisting of nitrogen containing solvents selected from formamide, dimethylformamide, dimethylacetamide and pyridine, cyclic ether compounds selected from tetrahydrofuran, and dioxane, sulfur containing solvents selected from dimethylsulfoxide and dimethyl sulfone and water soluble ketones.

9. A method according to claim 1, wherein said filaments are obtained by extruding a viscose containing 2 to 8 % total alkali and having a salt point of at least 16 into a coagulation bath containing 4 to 20 g/l formaldehyde, 20 to 250 g/l sodium sulfate, less than 0.3 g/l zinc sulfate and sulfuric acid in a concentration as shown by the following equations:

Minimum concentration of sulfuric acid (g/l) = 3A + 8

Maximum concentration of sulfuric acid (g/l) = 8A + 16

wherein A is alkali concentration (%) in the viscose.

10. A method according to claim 1, wherein said filaments are obtained by extruding a viscose containing 2 to 8 % total alkali and 0.2 to 2 % formaldehyde based on the weight of the viscose and having a salt point of at least 16 into a coagulation bath containing 1 to 6 g/l formaldehyde, 20 to 250 g/l sodium sulfate, less than 0.3 g/l zinc sulfate and sulfuric acid in a concentration as shown by the following equations:

Minimum concentration of sulfuric acid (g/l) = 3A + 8

Maximum concentration of sulfuric acid (g/l) = 8A + 16 wherein A is alkali concentration (%) in the viscose.

11. A method according to claim 1, wherein said filaments are obtained by extruding a viscose containing 2 to 8 % total alkali and having a salt point of at least 16 into a coagulation bath containing 14 to 50 g/l sulfuric acid, 20 to 250 g/l sodium sulfate, less than 1 g/l zinc sulfate at a temperature of lower than 35° C and treating the resultant filaments with an aqueous solution containing 15 to 70 g/l formaldehyde.

12. A method according to claim 1 wherein the regeneration degree of the filaments before relaxation is 20 to 80 %.

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