METHOD OF MAKING REGENERATED CELLULOSE FILAMENTS

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This application is a continuation-in-part of United States application Ser. No. 104,789, filed April 24, 1961, and now abandoned.

The present invention relates to a novel method for the production of regenerated cellulose filaments and fibers of high tenacities, having excellent dimensional stability to repeated washings, a substantially circular cross-section, a microfibrillar structure (all core structure) similar to that of cotton as well as a high degree of orientation and good resistance to bending. More particularly, the invention relates to a process for spinning viscose which contains cellulose having a DP of 500 at least, a gamma number of 45—100, and a viscosity of 150—1000 poises, in a very dilute sulfuric acid bath containing sodium sulfate and substantially no zinc sulfate.

The improvement of the present invention resides in incorporating formaldehyde in the viscose immediately prior to spinning (e.g., injected at the head of the spinning frame) or to the dilute spinning bath, which unexpectedly retards regeneration, whereby filaments with homogeneous, stable microfibrillar structure (all core structure) are formed, showing a substantially circular cross-section as well as a smooth, regular, uniform surface.

Therefore, it is a primary object of the present invention to provide an improved process for the production of regenerated cellulose filaments and fibers, the improvement being the addition of formaldehyde, either to the viscose immediately prior to spinning or to the dilute spinning bath, which formaldehyde functions to delay regeneration and thereby makes it possible to increase the stretching and orientation potential of filaments in the gelled state.

Another object of the present invention is to provide a process for the production of regenerated cellulose filaments and fibers which process involves the spinning of viscose which contains cellulose having a DP of at least 500, a gamma number of 45—100 and a viscosity of 150—1000 poises, in a dilute bath containing a small amount of sulfuric acid and sodium sulfate with substantially no zinc sulfate—e.g., 0.001 gram per liter to 1 gram per liter.

Still another object of the present invention is to provide a process for the production of regenerated cellulose filaments and fibers which process involves the spinning of viscose which contains cellulose having a DP of at least 500, a gamma number of 45—100 and a viscosity of 150—1000 poises, in a dilute bath containing a small amount of sulfuric acid and sodium sulfate with substantially no zinc sulfate—e.g., 0.001 gram per liter to 1 gram per liter.

Other objects of this invention will appear hereinafter.

In recent years, a great deal of work has been done in Japan, France and Switzerland on the development of fibers of regenerated cellulose having a stable microfibrillar structure. The major developments in this field resulted from the use of spinning baths containing low acid and low sodium sulfate concentration at ambient temperature. The prior art processes comprise, in general, the use of cellulose pulps of high DP whose depolymerization is limited to a minimum when preparing the viscose. Furthermore, large quantities of carbon disulfide are used, resulting in high gamma numbers. The spinning baths being used were approximately 10—30 grams preferably about 15 grams of sulfuric acid per liter, limited quantities of sodium sulfate and substantially no zinc sulfate.

These prior art baths are known in the art as dilute baths. The more concentrated baths, that is, baths containing higher amounts of sulfuric acid and/or sodium sulfate are conventionally known as Muller baths.

Inasmuch as the temperature utilized in the dilute bath is low and the amount of sulfate and acids is relatively small, only coagulation of the cellulose xanthate and substantially not regeneration of the cellulose takes place. The filaments of cellulose xanthate are then subjected to high stretch and, if desired, passed through a hot aqueous bath.

In contrast to the dilute bath, both coagulation and regeneration take place in the more concentrated Muller bath. Moreover, it has been proposed to add formaldehyde to the more concentrated baths (e.g., Muller baths) to prolong the regeneration period, with the thought that it forms a complex with the cellulose xanthate, and keeps the filaments in a metastable, stretchable state while they are being stretched, permitting uniaxial orientation of the crystalline elements being developed during regeneration.

The filaments obtained from a Muller bath are of the "all skin" or "skin-core" type and do not have any of the superior qualities of the filaments produced from a dilute bath as in the present invention. It was highly unexpected in accordance with the present invention that by the addition of formaldehyde to a viscose having a high DP and viscosity of 150—1000 poises or to a dilute bath, regeneration could be delayed so as to increase considerably the stretching and orientation of the filaments in the gelled state. Moreover, it was discovered that by virtue of the precise conditions of the present invention, that the addition of formaldehyde either to the dilute bath or to the viscose immediately prior to spinning, the disadvantages of the prior art were avoided.

It has been found when utilizing a dilute bath and a viscose having the general characteristics of this invention, that crystallization of the regenerated cellulose takes place during the coagulation with formation of a microfibrillar structure. The filaments and fibers thus produced are known in the art as polyacrylic or acrylic and they have excellent tenacity values with a high ratio of wet tenacity to dry tenacity. Furthermore, the polyacrylic filaments exhibit reduced swelling and are dimensionally stable under repeated washings and dryings. Their elongations are relatively small and the elasticity modulus in the wet state is relatively high. Therefore, the properties of these filaments are very similar to those of natural cellulose fibers. However, in order to obtain filaments and fibers having the required characteristics (high tenacity, micro-fibrillar "all core" structure, dimensional stability, etc.), the prior art processes such as described in U.S. Patents 2,607,955, 2,703,270 and 2,705,184 operate with baths having a low acid concentration and a low temperature, e.g., 10—30° C. as so as to insure that the gamma number of the filaments or fibers subjected to drawing is sufficiently high. It is under these circumstances that the strength of the filament in the gel state is relatively low and breakage of the filaments occurs. Moreover, even though higher concentrations of acid may facilitate spinning, said higher concentrations were found detrimental to the properties of the filament.

In accordance with the present invention, it was unexpectedly found that by the addition of formaldehyde to the viscose immediately prior to spinning (injected at the head of the spinning frame) or to the dilute spinning bath, it is possible to delay still further regeneration, so as to considerably increase the stretching and orientation potential of filaments in the gelled state. It is known in the art that an increase in orientation is generally accompanied by a reduction in transverse strength, that is, by a greater fragility to friction. However, in accordance
with the present invention, it was unexpectedly discovered that the improved orientation, by virtue of slowing down of the regeneration by the addition of formaldehyde, does not diminish substantially the transverse strength. Thus, the filaments obtained in accordance with the present invention are not fragile while they have very high tenacity values. It has also been found that when spinning in the presence of formaldehyde in accordance with this invention it is possible to use a somewhat more concentrated acid bath, and this has the advantage of improving the tenacity of the filaments in the gel state as well as permitting higher spinning speeds. Thus, the gamma number of the filaments at the outlet from the first bath is roughly higher for the purposes of the present invention as compared to similar processes which do not utilize formaldehyde. This is made clear from the following table which incorporates data, from the next Example 1:

| Bath containing 15 grams per liter of sulfuric acid and 1.5—9% total caustic soda, and no formaldehyde | 70 | 10 |
| Bath according to the present invention | 75 | 23 |

In accordance with the present invention, a viscose is utilized which contains at least 3% cellulose, from 1.5—9% total caustic soda, and no formaldehyde. Furthermore, it is essential that the sum of the sulfuric acid and sodium sulfate concentrations in the first bath does not exceed the range of 8—75 grams per liter. When the formaldehyde is added to the dilute spinning bath, it must be added in the range of 1—40 grams per liter of the bath. However, the formaldehyde may be incorporated in the viscose immediately prior to spinning and when added in this manner it should be within the range of 1—40 grams per kilogram of viscose. Furthermore, the formaldehyde may be added simultaneously to the viscose immediately prior to spinning and to the first dilute spinning bath. The total amount of formaldehyde when added in this manner should not exceed 40 grams per liter of the bath. The invention has substantially eliminated zinc sulfate from the spinning bath—that is, the bath may contain zinc sulfate in the amount of 0.001 gram per liter to 1 gram per liter. The bath temperature is preferably within the range of 10—30°C.

Accordingly, this invention is primarily based upon the discovery that by the addition of formaldehyde to the viscose immediately prior to spinning or to the first spinning bath, regeneration may be substantially slowed down with consequent increase in stretchability whereby a filament having excellent dimensional stability and tenacity may be obtained. As was pointed out previously, it is critical to the successful operation of this invention that the viscose have a viscosity of 150—1000 poises. It was found that lower viscosities are utilized with baths of low acid and low sulfate concentrations (within ranges of this invention) it is very difficult, if not impossible, to spin. In fact, prior art processes which utilized lower viscosities must spin their viscose into a bath of higher concentration than that of the present invention. Moreover, it was found that when spinning a low viscosity viscose (e.g., lower than 150 poises) under the conditions of the present invention, while spinning at a very low spinning speed to avoid difficulties, the filaments obtained were of irregular contour, non-uniform in cross-section and did not have a smooth, non-crunched surface or tenacities of the filaments produced in accordance with the present invention. Therefore, filaments produced from low viscosity viscose are not industrially acceptable as are the filaments from this invention. Also, it is the low overall concentrations used in this invention which lead to the formation of the highly swollen filaments obtained herein. Higher bath concentrations result in much less swollen filaments—i.e., the cohesion of the filaments would be too low. It is the high initial gel swelling of the present invention which is responsible for the characteristic structure of the filaments produced herein.

In accordance with the present invention, the filaments obtained from the first bath may be stretched by preferably over 200% and the stretching action may take place in the first bath or in a second very hot acid bath, as well as during travel through the air between the first bath and the second. In the case of spinning rayon staple fiber, the tow coming from the second bath may be subjected to conventional treatments and degassed (fleeed from residual CS₂) in a third hot acid bath. Further, the tow may be cut in the acid state and the fibers then fixed in a solution from formaldehyde. The filaments are received on a bobbin but they may be subjected to treatments on thread advancing reels according to the continuous spinning process.

The filaments produced in accordance with the present invention have a very high tenacity of at least 5 g./den. in the conditioned state, 4 g./den. in the wet state, as well as a high modulus of elasticity evidenced from an elongation in the wet state of less than 3% under a load of 0.5 g./den. As described hereinabove, the filaments have an "all core" structure and have a substantially round cross-section, that is, a smooth, even regular contour and their swelling degree, which is a function of the spinning conditions, is commonly less than 50%.

The determination of the structure of the filaments was carried out according to a technique similar to that of one which is described by M. Merchant & S. Lee in Textile Research Journal, December 1945, page 443. 8 micron thick cross sections embedded in paraffin, and adhering on a thin glass slide were:
(a) Dyed with a 2% solution of "Victoria Blue BS," at ordinary temperature for ten hours;
(b) Washed a few seconds with distilled water and then with xylene at 5—10°C. to remove the excess blue dye from the slide and the cross-sections;
(c) Dyed with a 0.2% solution of "Calconine Brilliant Yellow Concentrated" at ordinary temperature for ten hours; and
(d) Rinsed with xylene and then dried.

Under these conditions, the skin of the filaments is dyed blue, while the core is dyed yellow.

The filaments produced in accordance with the instant invention and dyed with this technique show an "all core" structure and differ completely from filaments produced from the more concentrated Muller baths, those filaments showing an "all-skin" or a "skin-core" structure.

The filaments obtained in accordance with the present invention are nearer to cotton than other filaments of regenerated cellulose. Furthermore, X-ray examination as well as birefringence measurements reveal an extremely oriented structure has been found in the filaments with a high degree of orientation the filaments have a good resistance to repeated bending. It has also been found that the fibers are extremely stable to and are not substantially modified by treatment with 6% caustic soda, whereas...
5. under the same conditions threads of ordinary rayon are considerably disorganized and even destroyed. Thus, fabrics made from the filaments of the present invention have excellent dimensional stability when subjected to repeated washings. It is believed that the alkali resistance of the fibers of the present invention is due to the microcrystalline structure of the filaments for it has been found that other rayon filaments having the same high DP are readily attacked by caustic soda whereas the fibers of the present invention are not.

The invention will be further described by means of the following specific examples which are given for illustration only and not in any way limiting. The invention covered by the examples which do not depart from the underlying idea of the invention, that is, the invention is equally applicable to the production of other articles from regenerated cellulose, such as foils, coarse fibers, cords, films, etc.

EXAMPLE I

Wood pulp having a high content of alpha cellulose was soaked for 30 minutes in caustic soda at 250 g./liter at 20° C. and pressed to obtain a three-fold increase in weight relatively to the alpha cellulose. After a very short period of ripening, the alkali cellulose was sulphurated with 55% of carbon disulphide (in relation to the alpha cellulose), and the xanthate formed was dissolved in dilute caustic soda so as to obtain a viscose containing 6.5% of cellulose and 5.5% of caustic soda. Surface-active agents were incorporated in this viscose in a conventional manner, facilitating filtration and preventing the blockage of the holes in the spinning dies. At the moment of spinning, the viscose had a viscosity of 500 poises, a gamma number of 75, and the cellulose contained in the viscose had a DP of 530.

The viscose was spun by means of a spinneret having 2000 holes of 7/100 of a millimetre in a first bath containing 25 g./liter of sulphuric acid and 15 g./liter of sodium sulphate at a temperature of 20° C. To this bath was added 10 g./liter of formaldehyde and a suitable surface-active agent such as lauryl pyridinium chloride. Spinning was carried out with a length of travel in the bath amounting to 400 cm. and with a stretch of 25%. When issuing from the first bath, the speed of the tow was 10 m./minute; its gamma number being 23.

The tow was then passed into a second regeneration bath containing 20 g./liter of sulphuric acid and 10 g./liter of sodium sulphate at a temperature of 93° C., and at the same time was subjected in this bath to a stretch of 200%, which gives a total stretch of 275%. The length of the tow before travel through this bath is 150 cm. The tow is finally wound under tension on a bobbin. After the usual treatments of de-acidification, washing, desulphurization and oiling, a thread was obtained which had the following characteristics:

<table>
<thead>
<tr>
<th>Unitary count</th>
<th>den.</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tenacity in the conditioned state</td>
<td>g./den.</td>
<td>6.7</td>
</tr>
<tr>
<td>Elongation in the conditioned state</td>
<td>percent</td>
<td>5.4</td>
</tr>
<tr>
<td>Elongation in the wet state</td>
<td>do.</td>
<td>5.1</td>
</tr>
<tr>
<td>Swelling</td>
<td>do.</td>
<td>45</td>
</tr>
</tbody>
</table>

EXAMPLE II

This example is given to fully illustrate the criticality of the viscosity of the viscose used in the process of the present invention.

A viscose was prepared in accordance with the procedure set forth in Example I wherein the cellulose concentration was 4.5% and the caustic soda concentration was 5.5%. As a result of the lower concentration of cellulose as compared with the viscose of Example I, the viscosity of the viscose was only 70 poises; however, the other characteristics were identical with those of Example I, e.g., DP of 530, gamma number of 75, etc.

The viscose was extruded through a spinneret of 2000 holes of 7/100 mm. in the same bath as used in Example I, that is, a bath containing 25 grams of sulphuric acid, 15 grams of sodium sulphate, and 10 grams of formaldehyde per liter at a temperature of 20° C.

It was found that it was impossible to spin at a speed of 10 meters/minute (exit from the first bath) as in Example I. Further, the slightly gelified viscose did not have the necessary cohesion to enable filaments to be drawn and stretched outside of the bath. Moreover, the viscose jets formed at the spinneret exhibited a strong tendency to stick together.

In order to overcome this result, it was necessary to reduce the spinning speed down to a value of 1 to 2 meters/minute at the exit of the first bath. However, the reduction in spinning speed in order to achieve favorable results makes the process unacceptable from an industrial standpoint.

The process of the present invention overcomes the disadvantages illustrated herein for it was unexpectedly found that by employing a high viscosity (e.g., at least 150 poises) the gelified filaments formed had sufficient cohesion so that they could be superfebrably coagulated without rupture. Also, the filaments could be drawn outside the first bath at a speed in order of 10 meters/minute.

EXAMPLE III

The following example clearly shows that in accordance with this invention, filaments of 2, 3, 5, and even 10 denier may be spun having a substantially round cross-section of regular contour.

The viscose and first dilute bath used were exactly the same as used in Example I. The viscose was spun by means of a spinneret having 2000 apertures of 39/100 of a millimeter in the first bath under exactly the same conditions as Example I. The total stretch was 260% and the filament properties were as follows:

<table>
<thead>
<tr>
<th>Denier</th>
<th>2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tenacity, dry</td>
<td>g./den.</td>
</tr>
<tr>
<td>Elongation, dry</td>
<td>percent</td>
</tr>
</tbody>
</table>

EXAMPLE IV

Example I was repeated except that a solution of formaldehyde was injected into the viscose immediately prior to spinning so that this viscose contained 20 g. of formaldehyde per kilogram. No formaldehyde was added to the first bath. In these conditions, the spinning equilibrium was about the same as in Example I. As a result of this experiment, a thread was obtained which had substantially the same characteristics as the thread formed in Example I.

EXAMPLE V

A viscose having a composition of 5% of cellulose and 2.4% of caustic soda was spun by means of a spinneret having 18,000 holes each of 7/100 of a millimeter, in a first bath containing 28 g./liter of sulphuric acid and 19 g./liter of sodium sulphate, at a temperature of 19° C.

To this bath was added 10 g./liter of formaldehyde and suitable surface-active agents. The tow formed was passed through a second regeneration bath, the stretches, the distance through the bath and the spinning speeds being substantially the same as those indicated in Example I. Finally, the tow passed through a third, hot bath for degasifying and cut in the acid state. After finishing, fibers were obtained which had the following characteristics:

<table>
<thead>
<tr>
<th>Unitary count</th>
<th>den.</th>
<th>1.35</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tenacity in the conditioned state</td>
<td>g./den.</td>
<td>6.15</td>
</tr>
<tr>
<td>Elongation in the condition state</td>
<td>percent</td>
<td>8.9</td>
</tr>
<tr>
<td>Elongation in the wet state</td>
<td>do.</td>
<td>9.6</td>
</tr>
</tbody>
</table>

Swelling | do. | 49 |
EXAMPLE VI

Example V was repeated except that a solution of formaldehyde was injected into the viscose immediately prior to spinning, so that this viscose contained 15 grams of formaldehyde per kilogram of viscose. No formaldehyde was added to the first bath. As a result of this experiment, a thread was obtained which had substantially the same characteristics as the thread formed in Example V.

EXAMPLE VII

A viscose containing 5% of cellulose and 2.5% of caustic soda was spun through a tube by means of a spinneret having 40 holes of 1/200 of a millimetre, into a first bath containing 30 g./liter of sulphuric acid, 17 g./liter of sodium sulphate and 5 g./liter of formaldehyde, at a temperature of 23° C. The length of travel in the first bath was 450 cm. and the stretch was 35%. The thread issued from the first bath at a speed of 20 m./minute and was then subjected to a stretch of 190% in a second hot bath similar to that of Example I. The thread, which now had a speed of 58 metres per minute was subjected successively, on two-cage bobbins in parallel spirals, to de-acidification, washing and desulphurization treatments. It was finally dried and twisted, all these operations being carried out continuously. Under these circumstances, a thread of 50 deniers was obtained, having the following features:

Unitary count ------------------------------- 1.25
tenacity in the conditioned state -------------- g./den. -- 6.30

tenacity in the wet state -------------- g./den. -- 5.2

elongation in the conditioned state ------- percent -- 6

Elongation in the wet state --------------------- 7

Swelling ------------------------------- 52

EXAMPLE VIII

Example VII was repeated except that a solution of formaldehyde was injected into the viscose immediately prior to spinning so that this viscose contained 15 grams of formaldehyde per kilogram of viscose. No aldehyde was added to the first bath. As a result of this experiment, a thread was obtained which had substantially the same characteristics as the thread formed in Example VII.

EXAMPLE IX

Example VIII was repeated except that the formaldehyde was injected to the viscose in the amount of 20 grams per kilogram. As a result of this experiment, the thread obtained had substantially the same characteristics as the thread formed in Example VII.

EXAMPLE X

Example VII was repeated except that the first bath contained 10 grams per liter sulphuric acid and 50 grams per liter of sodium sulphate. The other conditions of Example VII were repeated, and, as a result, the thread formed had substantially the same characteristics as the threads formed in Example VII.

The threads and fibers described herein are essentially suitable for textile uses, but their features, more particularly high tenacity and high modulus of elasticity, also make them suitable for certain technical applications in particular in the rubber industry.

The invention claimed is:

1. In a process for the production of filaments of regenerated cellulose, the improvement which comprises adding to a viscose immediately prior to spinning 1 to 40 grams per kilogram of formaldehyde, spinning said viscose which contains a cellulose whose DP is at least 500, and has a viscosity of 150 to 1000 poises, and a gamma number of 45 to 100 into a first dilute bath containing about 8 to about 35 grams per liter of sulphuric acid, about 0 to 65 grams per liter of sodium sulphate, the sum of the sulphuric acid and sodium sulphate concentrations being 8 to 75 grams per liter, and about 0.001 to .1 gram per liter of zinc sulfate, at a temperature between 10° C. and 30° C., to produce filaments, and then passing the filaments into a second hot regeneration bath and stretching said filaments at least 100% of their length at a stage prior to removal from said second bath, and finishing said stretched filaments whereby the filaments obtained have a very high tenacity both in the conditioned state and in the wet state, excellent dimensional stability, high modulai of elasticity in the wet state, a swelling value less than 55% and a uniform substantially round cross section as well as a smooth, regular surface contour.

2. A process according to claim 1 wherein the formaldehyde is added to the viscose immediately prior to spinning as well as to the first dilute spinning bath.

3. The process according to claim 2 wherein the amount of formaldehyde added to the viscose and first dilute bath is 10 grams per kilogram and 5 grams per liter, respectively.

4. A regenerated cellulose filament produced in accordance with the process set forth in accordance with the process of claim 1.

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