FIG. 1

DYE EXHAUSTION (%)

0  2  4  6  8  10
Na_2SO_4(g/L)

CH_2O 75g/L

40
30
FIG. 2

FIG. 4

FIG. 3
HIGHLY CRIMPED POLYNOSEC FIBERS

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ABSTRACT OF THE DISCLOSURE

A viscose having a $\gamma$-value of at least 50 is extended into a coagulation bath containing formaldehyde, and the resulting filaments are stretched in a second bath at 45° to 75° C. under a tension of up to 0.3 g./d. and then treated in a third bath containing alkali metal, alkaline earth metal and/or ammonium salts of sulfuric acid at a pH of 2.0 to 10.5 and a temperature of 30° to 70° C. The obtained high crimped polymeric fibers have an asymmetric structure with a core-stable layer positioned at the inside track of the crimp bend; the dye exhaustion is at least 40%, wet modulus is 0.5 to 1.8 g./d. and crimps are more than 10/25 mm.

This application is a division of application for U.S. Letters Patent Ser. No. 669,800, filed Sept. 22, 1967, now Pat. No. 3,574,812.

The present invention relates to improved highly crimped polymeric fibers and a process for producing the same.

Recently, there have been proposed many processes for producing polymeric fibers having excellent properties by extruding a viscose having high $\gamma$-value into a coagulation bath containing formaldehyde and stretching the resulting filaments in a hot dilute acid bath (second bath).

The filaments which have been withdrawn from the coagulation bath containing formaldehyde have high stretchability, and therefore when they are highly stretched in the second bath kept at a relatively high temperature, there are obtained fibers having high tenacity, high wet modulus and high resistance to water and alkali solutions.

The above-mentioned processes are disclosed in, for example, U.S. Pat. Nos. 2,937,070, 3,107,970 and 3,225,461, British Pat. Nos. 910,878, 993,786 and 1,027,153, French Pat. Nos. 1,266,492, 80,314,126,492, 1,302,294 and 1,351,736, and Belgian Pats. Nos. 602,660, 608,811 and 626,075.

On the other hand, when the filaments formed in the coagulation bath containing formaldehyde are stretched in the second bath at a relatively low temperature and under such a small tension as 0.3 g./d. or less and are then relaxed in a third aqueous bath, crimped polymeric fibers can be obtained.

Generally, fibers obtained by use of a coagulation bath containing formaldehyde have many such excellent characteristics as mentioned above. On the other hand, however, they are not sufficient in elongation and dyeability and are not satisfactory in knot tenacity and the like.

It has been found that in order to establish a method for improving fiber properties, it is extremely effective to adopt a process in which the filaments, obtained by extruding a viscose having a $\gamma$-value of at least 50 into a coagulation bath containing sulfuric acid, sodium sulfate and formaldehyde and then stretching the resulting filaments in a second bath kept at 45° to 75° C. under a tension of up to 0.3 g./d., are treated with an aqueous solution (third bath) containing an alkali metal salt of sulfuric acid, alkaline earth metal salt of sulfuric acid, ammonium salt of sulfuric acid or a mixture thereof, said third aqueous bath being kept at a pH of 2.0 to 10.5 and at a temperature of 30° to 70° C. The third bath may also contain a small amount of a sulfuric acid salt of zinc or cadmium.

When the filaments, which have been prepared by extruding a high $\gamma$-value viscose into a coagulation bath containing sulfuric acid, sodium sulfate and formaldehyde and then stretching the resulting filaments in a second bath, are introduced into an aqueous solution of, for example, sodium sulfate, the filaments unexpectedly swell to a great extent and they are sometimes dissolved after a period of time. Such a phenomenon is observed not only in the case of sodium sulfate but also in the case of sulfuric acid salts of other alkali metals, alkaline earth metals or ammonia. Such swelling action is greatly affected by the pH and temperatures of the salt solutions employed. Therefore the pH and temperatures of the salt solutions to be used in the present invention should be within the ranges as described above. If the pH is less than 2.0, the diffusion of hydrogen ion into the fiber becomes marked, whereby the effective swellings of fibers into the salt employed is restrained. On the other hand, if the pH is more than 10.5, the fiber is swelled to a great extent and is markedly lowered in tenacity. Moreover, even when, in the above case, a sulfuric acid salt of zinc or cadmium is incorporated into the salt solution, the specific action described hereafter cannot be obtained. As to the temperature, it may be said that the higher the temperature, the stronger the swelling action of the salt. However, if the temperature is excessively high, regeneration of the fiber progresses to make difficult the swelling of the fiber.

The preferred treatment temperature is within the range of 30° to 70° C. It has also been found that when an aqueous solution of a salt having a swelling action on fiber, as mentioned above, is incorporated with such a slight amount as less than 0.5 g./l. of a sulfuric acid salt of zinc or cadmium, the swelling of the fiber is suitably controlled and the fiber properties are improved more effectively.

In practicing the present process on a commercial scale, there is ordinarily used as a third bath an aqueous solution containing up to 50 g./l. of sodium sulfate and up to 1 g./l. of sulfuric acid. The third bath, however, desirably contains, additionally, up to 0.5 g./l. of zinc sulfate.

In the present invention, only fibers which are produced using a coagulation bath containing formaldehyde can be treated with an aqueous salt solution and the stretched filaments are still high in $\gamma$-value. From the above, it is concluded that the swelling or dissolution of the fibers by action of said salts is ascribable to behavior peculiar to cellulose hydroxyethyl-xanthate, which is a reaction product of cellulose xanthate and formaldehyde.

In the accompanying drawings, FIG. 1 is a graph which expresses the above general relationship, and FIG. 2 shows the cross section of the fibers obtained by treatment in accordance with the present invention.

FIGS. 3 and 4 show the side view of the present fiber and a conventional fiber.

In FIG. 1, the horizontal axis is graduated to show the sodium sulfate concentration in the third bath, while the vertical axis shows the dye exhaustion as a characteristic representing the swelling effect. The solid line shows the case where a viscose containing 7% of cellulose and 4% of alkali and having a $\gamma$-value of 80 and a viscosity of 260 poises is extruded into a coagulation bath containing 26 g./l. of sulfuric acid, 75 g./l. of sodium sulfate, 0.1 g./l. of zinc sulfate and 7.5 g./l. of formaldehyde and kept at 25° C., and the resulting filaments are stretched...
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to 380% in a second bath kept at 70°C and are then treated in a third aqueous bath containing up to 10 g./l. of sodium sulfate and 0.1 g./l. of zinc sulfate and kept at 70°C. The dotted line shows the case where the treatments are effected under the same conditions as above except that no formaldehyde is contained in the coagulation bath and the stretch ratio in the second bath is 150%. From this graph, it is clear that no swelling effect is displayed at all when the coagulation bath contains no formaldehyde. Conditions for measuring the dye exhaustion are as follows:

Sample: 3 g.
Japonol Brilliant Blue 6BXX: 0.3% (o.w.f.)
Sodium sulfate: 20% (o.w.f.)
Batch ratio: 1:100
Temperature and time: 45°C. ×20 minutes

The absorbance of the residual liquid is measured by means of a photoelectric colorimeter to calculate the dye exhaustion.

In FIG. 2, black parts show the skin-stained layer. For skin-staining, fibers are stained using the following conditions followed by washing through the alcohol series.

Japonol Brilliant Blue 6BXX (C.I. Direct Blue 1): 1% (o.w.f.)
Sodium chloride: 10% (o.w.f.)
Temperature and time: 100°C. ×30 minutes

In FIGS. 3 and 4, black parts show the core-stained layer. For core-staining, fibers are stained using the following conditions, followed by washing with water and dehydration.

Solophenyl Fast Blue Green B.L. (C.I. Direct Green 27): 1% (o.w.f.)
Sodium sulfate: 0.3% (o.w.f.)
Temperature and time: Ambient temperature ×5 hours

When the treating method of the present invention is applied to filaments which have been stretched in the second bath under a tension of less than 0.3 g./d., the resulting fibers are more improved, without any substantial lowering in tenacity, in lateral properties of fiber, such as elongation, knot tenacity and abrasion resistance, and in dyeability as well as in degree of crimp.

The present process will be explained in more detail below.

The γ-value of the viscose employed is required to be at least 50, preferably at least 65 (corresponding to a salt point of at least 16). If the γ-value is lower than said value, the effect of formaldehyde in the coagulation bath is not sufficient and no satisfactory crimps can be developed.

The formaldehyde concentration of the coagulation bath is preferably 4 to 15 g./l. It is particularly desirable that the sulfuric acid concentration of the coagulation bath is within the range defined by the following equations:

Minimum concentration of sulfuric acid (g./l.) = 3.4 + 4 Maximum concentration of sulfuric acid (g./l.) = 8.4 + 16

wherein A is the total alkali concentration in viscose which is preferably 2 to 8%. The concentration of sodium sulfate is preferably 20 to 250 g./l., and that of zinc sulfate, if it is to be incorporated, is desirably up to 0.3 g./l.

The filaments withdrawn from the coagulation bath are then stretched in the second bath. In this case, the temperature of the bath and the tension applied to the filaments during stretching are the most important factors. The temperature of the second bath is within the range of 45°C to 75°C. If the bath temperature is out of said range, no excellent crimps can be developed. The tension applied to the filaments during stretching should be less than 0.3 g./d. If the tension is more than 0.3 g./d., no highly crimped fibers can be obtained. The second bath preferably contains a small amount of sulfuric acid, in view of the subsequent treatment. The bath may also contain small amounts of salts and formaldehyde.

The filaments, which have been stretched in the above manner, are then relaxed, either as such or after cutting to staples, in a third bath comprising an aqueous salt solution, whereby the fibers undergo swelling, action and, at the same time, develop markedly fine crimps. In this case, the temperature of the third bath is 30°C to 70°C. If the temperature is below 30°C, the swelling effect is low, while if the temperature is above 70°C, no excellent crimps are developed. The fibers which have developed crimps are then transferred to a high temperature acidic bath to complete regeneration.

The fibers obtained according to the above-mentioned process have such characteristics as described below.

The cross section and side view of the fiber are in such a specific form as shown in FIGS. 2 and 3, respectively, and in the fibers, the core-stainable layer is biased. Thus, the fibers have a heterogeneous structure as if they were conjugate fibers. The crimp of the fibers is in a spiral form but, unlike the case of a conventional crimped staple fiber as shown in FIG. 4, the core-stainable layer is always positioned at the inside track of the crimp bend. In water, therefore, the crimp is straightened to a certain extent due to greater swelling of the core-stainable layer, but is completely restored on drying. That is, the fiber of the present invention has such a property as that of wool having so-called water reversible crimps. In contrast thereto, in the case of the conventional conjugate fibers or the so-called broken skin-type viscoso crimped staples, the skin-stainable layer is always positioned at the inside track of the crimp bend. Further, in the case of the conventional crimped viscoso staples also, the thicker side of the skin-stainable layer is positioned at the inside track of the crimp bend. These fibers, therefore, are different in behavior to water from the fibers of the present invention. It is considered that the excellent crimp properties of the present fibers are derived from the aforesaid specific structure, which is entirely different from that of the conventional crimped viscoso staples.

The fibers of the present invention are not only excellent in crimp properties but also have excellent mechanical properties. Tenacity and wet modulus of the fibers are far higher than those of the conventional common crimped viscoso staples. Particularly, the wet modulus at 5% elongation of the present fibers is, in general, 0.5 to 1.8 g./d. or more. Therefore, the fibers are excellent in dimensional stability and can withstand repeated washing. They are also highly high in knot tenacity and excellent in abrasion resistance. The water retention of the fibers is equal to or somewhat higher than that of the recent polyacryl fibers but the water resistance and dimensional stability thereof are sufficiently high. Excellence in dyeability is also a great characteristic of the fibers. Concretely, the fibers have a dye exhaustion of more than 40%, ordinarily in the range of 45 to 85%, a wet tenacity of 1.8 to 4 g./d., a wet modulus at 5% elongation of 0.5 to 1.8 g./d., and crimps of more than 10/25 mm.

Owing to those superior crimp and mechanical properties, the fibers can be used in a wide variety of fabrics with or without synthetic or cotton fibers. Fabrics converted from the fibers have comfortable hand, high slip-resistance, high dimensional stability and superior mechanical properties.

The following examples illustrate the present invention:

**EXAMPLE 1**

A viscos containing 6.5% of cellulose and 4.5% of total alkali and having a viscosity of 170 poises, a salt point of 21 and a γ-value of 82 was extruded into a coagulation bath containing 35 g./l. of sulfuric acid, 75 g./l. of sodium sulfate and 7 g./l. of formaldehyde and kept at 25°C. The filaments withdrawn from the co-
agulation bath were immediately stretched to 300% the original length of the filaments under a tension of 0.05 g./d. in a second bath kept at 60° C. and containing 2 g./l. of sulfuric acid. Thereafter, the filaments were relaxed in a third bath containing 5 g./l. of sodium sulfate and 0.1 g./l. of zinc sulfate and kept at 50° C. and at a pH of 6.8 to develop crimps. The γ-values of the filaments just before entering the second and third baths were 65 and 57, respectively. Subsequently, the regeneration of the filaments were completed in an aqueous bath containing 5 g./l. of sulfuric acid and kept at 85° C. and were then scoured according to a conventional procedure. Fiber properties of the thus obtained fibers are shown in Table 1-(A), and the cross section of the fiber after dyeing are shown in FIG. 2.

For reference, fibers (B) were produced in the same manner as above, except that the third bath contained no sulfates and was kept at 50° C. Fiber properties of these fibers are as shown in Table 1-(B).

**TABLE 1**

<table>
<thead>
<tr>
<th>Denier (g/1000 m)</th>
<th>Wet tenacity (g/1000 m)</th>
<th>Conditioned tenacity (g/1000 m)</th>
<th>Wet elongation (percent)</th>
<th>Conditioned elongation (percent)</th>
<th>Wet modulus at 5% elongation (g/1000 m)</th>
<th>Conditioned modulus at 5% elongation (g/1000 m)</th>
<th>Number of crimps per 25 mm.</th>
<th>Degree of crimp (percent)</th>
<th>Dye exhaustion (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. ........................</td>
<td>3.0</td>
<td>3.7</td>
<td>2.8</td>
<td>15</td>
<td>1.6</td>
<td>1.1</td>
<td>24</td>
<td>28</td>
<td>61</td>
</tr>
<tr>
<td>B. ........................</td>
<td>3.0</td>
<td>3.9</td>
<td>3.1</td>
<td>10</td>
<td>1.8</td>
<td>1.4</td>
<td>17</td>
<td>20</td>
<td>55</td>
</tr>
</tbody>
</table>

**EXAMPLE 2**

A viscose containing 7% of cellulose and 4.5% of alkali and having a viscosity of 320 poises, a salt point of 22 and a γ-value of 84 was extruded into a coagulation bath containing 37 g./l. of sulfuric acid, 80 g./l. of sodium sulfate and 8 g./l. of formaldehyde and kept at 23° C. The filaments withdrawn from the coagulation bath were immediately stretched to 290% the original length of the filaments under a tension of 0.045 g./d. in a second bath containing 1 g./l. of sulfuric acid and kept at 60° C. Thereafter, the filaments were relaxed in a third bath containing 0.2 g./l. sulfuric acid, 10 g./l. of sodium sulfate and 0.1 g./l. of zinc sulfate, and kept at 60° C. at a pH of 3.4 to develop crimps. Subsequently, the regeneration of the filaments were completed in an aqueous bath containing 5 g./l. of sulfuric acid and kept at 85° C. The γ-values of the filaments just before entering the second and third baths were 66 and 59, respectively. Fiber properties of the thus obtained fibers are shown in Table 2-(A).

For reference, fibers (B) were produced in the same manner as above, except that the third bath employed contained only 10 g./l. of sulfuric acid and kept at a pH of 1.4. Fiber properties of these fibers are shown in Table 2-(B).

What is claimed is:

1. An improved highly crimped polynosic fiber comprising a heterogeneous structure asymmetric in the cross-sectional direction of the fiber, wherein a core-stainable layer is always positioned at the inside track of the crimp bend, said fiber having a dye exhaustion of at least 40%.
2. A fiber according to claim 1, wherein the fiber has a wet tenacity of 1.8 to 4 g./d., a wet modulus at 5% elongation of 0.5 to 1.8 g./d. and crimps of more than 10/25 mm.

**References Cited**

UNITED STATES PATENTS

3,419,652 12/1966 Kubota et al. 264—168

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