

March 29, 1955

R. R. JAMES
VISCOSE SPINNING PROCESS

2,705,183

Filed March 8, 1952

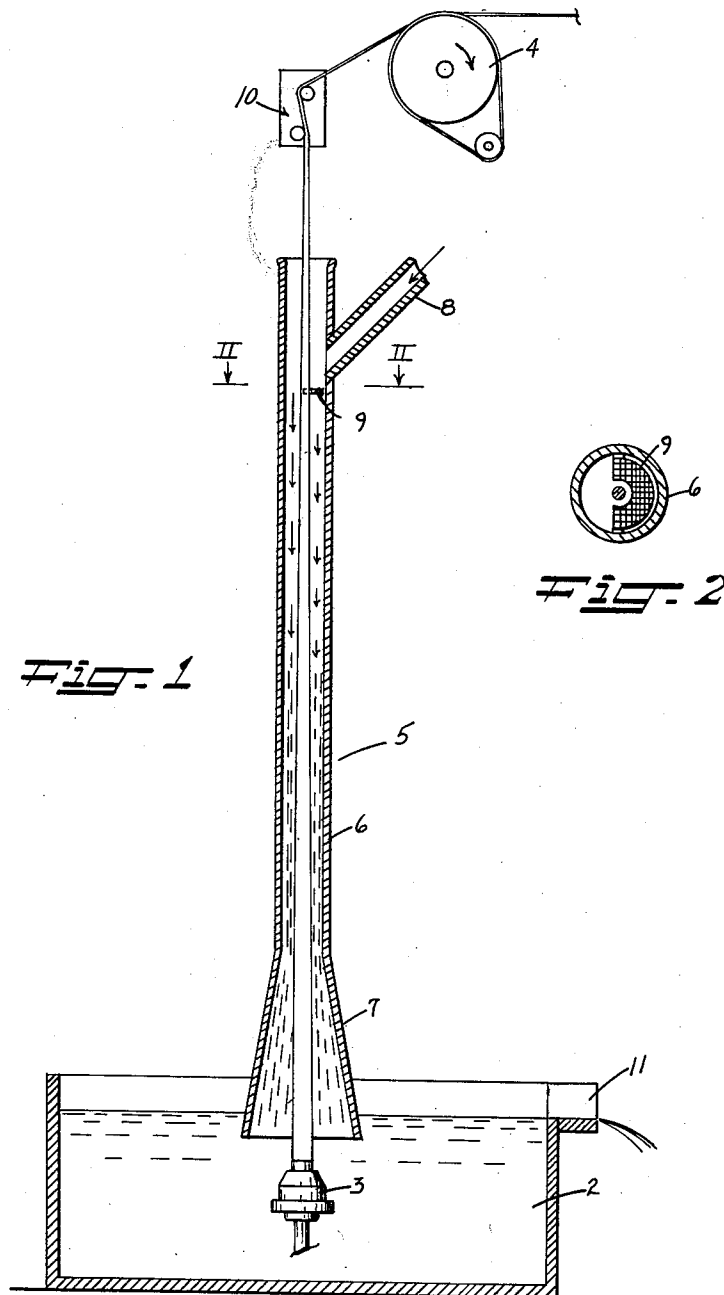


Fig. 1

Fig. 2

INVENTOR.
ROBERT R. JAMES
BY
Thomas R. O'Nalley
ATTORNEY.

1

2,705,183

VISCOSE SPINNING PROCESS

Robert R. James, New York, N. Y., assignor to American Viscose Corporation, Philadelphia, Pa., a corporation of Delaware

Application March 8, 1952, Serial No. 275,547

11 Claims. (Cl. 18—54)

This invention relates to the production of regenerated cellulose articles from viscose. More particularly, the invention relates to the production of regenerated cellulose filaments and yarn having high flexural strength from viscose.

In the conventional method for producing regenerated cellulose filaments and yarns from viscose, the viscose is extruded through a spinneret into a coagulating and regenerating bath comprising an aqueous solution of sodium sulfate and a relatively high proportion of sulfuric acid, such as 10 to 15%. Photomicrographs of the filaments formed in the conventional baths reveal that these filaments have a highly serrated or crenulated surface and comprise a well-oriented peripheral area or "skin" around an inner area or "core" which is relatively less oriented. The skin of these filaments or fibers can be accentuated by dyeing, since the skin and core portions dye differentially. Yarns comprising these normal skin- and core-type regenerated cellulose filaments are used for many purposes. However, when yarns are required for use under conditions involving severe flexing, for example when they are to be used in tire cords, it is desirable to provide filaments having a greater resistance to rupture on flexing than is exhibited by these normal filaments comprising a skin and core.

Regenerated cellulose filaments which, throughout their cross-section or for a major portion of their cross-section, exhibit a skin-type structure similar to the skin of the normal skin- and core filaments, and which comprise little or no core, have increased flexural strength as compared to the skin- and core filaments. In general, the greater the portion of the cross-sectional area having the skin-type structure, the higher is the resistance to rupture on flexing of the filaments.

It has been found that filaments having the skin-type structure throughout or for a major portion of their cross-section can be produced by extruding viscose into a coagulating and regenerating bath comprising an aqueous solution of sodium sulfate, zinc sulfate and an amount of sulfuric acid which is relatively small compared to the amount normally used. However, filaments formed in the low-acid bath are fragile and, unlike the normal skin- and core filaments, cannot be stretched for orientation and improvement in tenacity and extensibility without further treatment to condition them for such stretching.

It is an object of this invention to provide an improved method for producing strong regenerated cellulose filaments having a skin-type structure in cross-section. Other objects and various advantages of the invention will appear hereinafter.

It is known that when filaments or yarns are passed through a body of liquid moving in a direction opposite to the filaments, a frictional force is set up whereby the filaments or yarns undergo extension. The present method takes advantage of this frictional force to stretch and strengthen the fragile filaments set up in a low-acid coagulating and regenerating liquid as the coagulation and regeneration of the cellulose proceed, and under special conditions such that the moving liquid through which the filaments are passed is delivered directly to the liquid into which the viscose is extruded where it serves to set up streams of viscose emerging from the spinneret as distinct filaments having the skin-type cross-section.

In accordance with this invention, viscose is extruded through a spinneret into a relatively quiescent coagulating and regenerating liquid in the neighborhood of the spinneret comprising an aqueous solution of, by weight, from

2

2 to 5% preferably 4 to 5% of sulfuric acid, from 8 to 12% of zinc sulfate and an amount of sodium sulfate between 18% and the saturation limit, and the filaments thus formed are passed upwardly from the spinneret through a confined coagulating and regenerating liquid supplied to the system at a point spaced from the spinneret and flowing downwardly countercurrently to the filaments at a velocity which decreases gradually at the end of the confined path adjacent the spinneret, said countercurrent liquid comprising, at its point of supply to the system, an aqueous solution of 8 to 12% sulfuric acid, 8 to 12% zinc sulfate and at least 18% of sodium sulfate.

The countercurrent liquid is initially more strongly acid than the relatively quiescent liquid surrounding the spinneret, but by neutralization of sodium hydroxide carried by the advancing filaments, the acidity of the countercurrent liquid decreases progressively in the direction of its flow. The filaments thus advance from a coagulating and regenerating liquid of relatively low acidity upwardly through a coagulating and regenerating liquid of progressively increasing acidity in the direction of travel of the filaments, with progressive coagulation and regeneration of the cellulose. By controlling the velocity of the countercurrent liquid, it is possible to control the stretch imparted to the advancing filaments, and by varying the velocity of the countercurrent liquid along the confined path it is possible to vary the stretch imparted to the filaments at any point along the path of their advance from the spinneret. The filaments may be completely coagulated when they are withdrawn from contact with the countercurrent stream and the stretch imparted to them as a result of the drag exerted thereon by the moving liquid may be the only stretch to which the filaments are subjected. Or the filaments leaving the confined path may still be in plastic condition and may be stretched, for instance between godets or on a thread-storing, thread-advancing reel, after they are withdrawn from the confined path along which they are contacted by the countercurrent stream.

In practicing the invention, the initially more strongly acid coagulating and regenerating liquid is allowed to flow into the low-acid liquid into which the viscose is extruded, and the conditions are controlled so that as a result of the neutralization of sodium hydroxide carried by the filaments by the countercurrent liquid, the acidity of the countercurrent liquid is progressively reduced in the direction of its flow and by the time the countercurrent joins the liquid in the neighborhood of the spinneret, it has the same acidity as the liquid surrounding the spinneret. The system is thereby maintained at equilibrium and the countercurrent liquid is used to set up the viscose emerging from the spinneret without conditioning thereof.

In practice, the spinneret is supported face up in a vessel containing the low-acid coagulating and regenerating liquid, preferably near the surface of the liquid, for instance at a depth such that the distance between the spinneret face and the surface of the liquid is just sufficient to permit the liquid to set up the streams of viscose as individual filaments strong enough to be drawn away from the spinneret. This distance may be between a fraction of an inch, for example 1 cm., and 8 cm. It is important to avoid turbulence in the spinning liquid surrounding the spinneret due to the entry of the countercurrent liquid, and for this reason it is preferred to vary the velocity of the descending liquid so that it moves more slowly at the portion of its path adjacent to the spinneret than at the portions of the path spaced from the extrusion zone. Since the path of the countercurrent stream is defined by confining it in a suitable conduit supported above the spinneret the required reduction in the velocity of the countercurrent stream as it approaches the spinneret may be effected by increasing the cross-section of the end of the conduit nearest the spinneret.

In a preferred embodiment, the conduit to which the countercurrent liquid is supplied and through which the filaments are passed and acted upon by the countercurrent takes the form of an inverted funnel supported above the vessel in which the spinneret is located, with the edge of its conical portion projecting a short distance into the liquid surrounding the spinneret. The countercur-

3

rent stream flows downwardly through the stem or tubular portion of the funnel and enters the conical portion through which it flows at progressively and gradually decreasing velocity until it leaves the conical portion and flows into the vessel containing the spinneret. At this point, the velocity is reduced to the extent that turbulence in the liquid surrounding the spinneret is held at a minimum so that the viscose is extruded into relatively quiescent liquid. The reduction of the velocity of the countercurrent stream in the conical portion of the funnel also has the advantage that the filaments pass through the relatively slowly moving countercurrent liquid in the conical portion of the funnel before they enter the tube or stem of the funnel and are thereby strengthened before they are acted on by the liquid in the tube of the funnel, which moves downwardly at full countercurrent velocity and exerts a strong drag on the filaments. Other conditions being fixed, including the spinning speed and rate at which the countercurrent liquid is introduced into the tubular portion of the funnel, the cross-section and length of the tubular and conical portions of the funnel are selected to insure that the filaments are exposed to the action of the countercurrent liquid for a time interval between $\frac{1}{3}$ of a second and 3 seconds, and preferably between $\frac{1}{2}$ of a second and 1 second.

The flow of the initially more highly acid coagulating and regenerating liquid downwardly through the conduit may be produced by any suitable means such as a static head or a pump. In order that the stretch imparted to the filaments by the drag exerted on them by the countercurrent liquid will be uniform, it is desirable to maintain the velocity of the countercurrent stream constant at any point in the path of the advancing filaments once the spinning has been started. However, for lacing up the funnel and starting the collection of the filaments on a suitable collecting device, it is advantageous to cause the liquid in the funnel to move in the direction of travel of the filaments, and after the spinning has been initiated, and the collection device has begun to draw off the filaments, to reverse the flow of the liquid. Any suitable means may be associated with the system to permit the introduction of a suitable liquid into the conical portion of the funnel and cause the same to flow in the direction of extrusion until the apparatus has been laced up. For example, an aspirator may be provided at the top of the conduit.

Although the foregoing discussion has been in terms of filaments obtained by extruding the viscose through a spinneret provided with a multiplicity of orifices, single orifice spinnerets or jets may be used when it is desired to produce articles of very heavy denier, i. e., bristles, ribbons or the like.

The filaments may be collected and/or twisted by any suitable means. For example, they may be collected in a spinning box or wound on a swift, bobbin or other package core.

The temperature of the relatively quiescent low-acid coagulating and regenerating liquid surrounding the spinneret may be between 40 and 90° C., and when the bath is heated to the higher temperatures the viscose may be preheated and extruded into the hot bath at or near the temperature of the bath. The countercurrent liquid may be maintained at or near the temperature of the liquid into which the viscose is extruded or it may be maintained at a temperature higher or lower than the temperature of the liquid into which the viscose is extruded. Also, the temperature of the countercurrent may be different at different points along its flow through the conduit. Suitable means such as heating and/or cooling coils may be associated with the apparatus for controlling or regulating the temperature of the countercurrent liquid as desired.

The invention is illustrated in the accompanying drawing in which,

Fig. 1 is a diagrammatic showing of apparatus which may be used in carrying out the method; and

Fig. 2 is a view in cross-section taken on line II—II of Fig. 1.

In the drawing, Fig. 1 shows an apparatus consisting of a vessel 2 containing the low-acid aqueous coagulating and regenerating liquid. Spinneret 3 is supported face up below the level of the bath for extrusion of the viscose upwardly in a generally vertical direction. The filaments are withdrawn from vessel 2 by godet 4 driven by any suitable means, not shown, through an inverted

4

funnel indicated generally at 5 and comprising the tube 6 and conical portion 7, supported above the spinneret with its lowermost edge projecting into the liquid in vessel 2 and its longitudinal axis perpendicular to the center of the spinneret face so that the filaments are drawn directly into the funnel without being subjected to mechanical abrasion. For the usual spinning speeds between 40 and 70 meters per minute, other conditions being appropriately controlled, the tubular portion of the funnel may have a constant internal diameter between 0.95 cm. and 1.6 cm. and a length of from 40 cm. to 90 cm., and the conical portion of the funnel may taper outwardly from the tube to a maximum internal diameter of 6.4 cm. and have a length between 9 and 10 cm., in order to insure that the filaments are exposed to the countercurrent for a time interval between $\frac{1}{3}$ of a second and 3 seconds. The conical portion of the funnel is constructed, preferably, to provide a body of quiescent liquid in which the path for a yarn through the funnel extends approximately 1 to 8 centimeters. The more highly acid aqueous coagulating and regenerating liquid is introduced into the tube of the funnel near the end thereof away from the conical portion through a pipe 8. A distributor in the form of a semi-cylindrical screen 9 may be supported in the tube, adjacent the inner wall of the tube, so that the liquid introduced through pipe 8 passes through the distributor to contact the filaments advancing through the funnel without damage to the filaments. Excess liquid is removed from the filaments by the stripping device comprising a pair of stationary or rotary rods 10, and flows back along the filaments to the liquid introduced through pipe 8. Flow of the liquid in the funnel is essentially downward. By selection of the several interdependent conditions of spinning, as indicated hereinabove, the acidity of the countercurrent stream flowing into vessel 2 may be controlled so that it is the same as that of the liquid in vessel 2 at the start of operations, and the composition of the liquid surrounding the spinneret may be maintained constant throughout the spinning without additions to the system other than the initially more highly acid coagulating and regenerating liquid introduced into the funnel through pipe 8. Spent spinning liquid overflows vessel 2 at the overflow weir 11, and is forwarded to a suitable reconditioning or make-up system.

The following examples in which parts given are by weight are illustrative of the invention.

Example I

Apparatus as shown in the drawing was used. At the start of operations, vessel 2 was provided with a coagulating and regenerating liquid comprising an aqueous solution of 4% sulfuric acid, 8% zinc sulfate and 20% sodium sulfate. The spinneret 3 adapted to form a 490 filament, 1100 denier yarn was supported face up in the liquid, the distance between the spinneret face and the surface of the liquid being about $\frac{1}{4}$ cm. Viscose having a normal ball fall viscosity i. e. a ball fall viscosity of 35 seconds at 18° C., containing 6.6% of sodium hydroxide and 7.8% cellulose, and aged to a sodium chloride salt test value of about 5, was extruded through the spinneret at a rate of 200 gms. per minute. The filaments were drawn up through the inverted funnel 5 by godet 4 at a speed of about 47 meters per minute. The funnel comprised a tube having a constant internal diameter of 0.95 cm. and a length of 40 cm. and a conical portion tapering outwardly from the tube to a maximum internal diameter of about 6.4 cm. and having a length of 9 cm. Throughout the spinning, a coagulating and regenerating liquid comprising an aqueous solution of 10% sulfuric acid, 8% zinc sulfate and 20% sodium sulfate, was introduced into tube 6 through pipe 8 at a rate of 324 gms. per minute. It flowed downwardly to vessel 2 countercurrent to and in contact with the filaments and on reaching the relatively quiescent low-acid solution surrounding the spinneret had the same acidity as that solution.

Example II

The apparatus used was similar to that described in Example I except that the filaments were drawn up through the inverted funnel 5 by the godet 4 at a speed of about 70 meters per minute, and the funnel comprised a tube or stem having a constant internal diameter of 1.58 cm. and a length of 80 cm., and a conical portion which tapered outwardly from the end of the tube to a maximum internal diameter of 6.4 cm. and had a length

of 10 cm. Under these conditions the filaments were exposed to the countercurrent liquid in the tube for approximately 0.7 seconds.

The regenerated cellulose filaments produced under the conditions described were not of the usual skin-and-core type. Instead, the filaments were bulbous in cross-section and, throughout the cross-section, showed under microscopic examination a skin-type structure similar to that of the skin of the skin-and-core filaments obtained by conventional processes. The yarns comprising the bulbous filaments of skin-type cross-section exhibited high tenacity and excellent flexural strength.

In general, the percent and concentration of the ingredients named in the above examples are not critical and lie within the following ranges. The viscose solution may contain from 6 to 8% sodium hydroxide and 7 to 9% cellulose, and have a sodium chloride test value of 4 to 8. The coagulating and regenerating liquid may comprise, at the point of introduction to the funnel-shaped applicator, 8 to 12% sulfuric acid, 8 to 12% zinc sulfate and an amount of sodium sulfate between 18% and the saturation limit therefor within the liquid.

Since various changes and modifications may be made in the details set forth in the examples and discussion without departing from the spirit and scope of the invention, it is to be understood that the invention is not to be limited except as defined in the appended claims.

I claim:

1. The method of making regenerated cellulose filaments which comprises extruding viscose containing from 6 to 8% sodium hydroxide and 7 to 9% cellulose, and having a sodium chloride salt test value of 4 to 8 upwardly through a spinneret into an aqueous coagulating and regenerating liquid to form filaments, said liquid comprising a relatively quiescent portion in the neighborhood of the spinneret and a countercurrently flowing portion applied to the filaments at a point spaced from the spinneret, the relatively quiescent portion of the liquid comprising an aqueous solution of from 2 to 5% sulfuric acid, from 8 to 12% zinc sulfate and an amount of sodium sulfate between 18% and the saturation limit, and the countercurrently flowing portion of the liquid comprising, at its point of supply to the filaments, an aqueous solution of 8 to 12% sulfuric acid, 8 to 12% zinc sulfate, and at least 18% sodium sulfate, the filaments being in contact with the countercurrently flowing portion of the liquid for a time interval between one-third of a second and three seconds.

2. The method of claim 1 in which the distance the filaments travel through the relatively quiescent portion of the liquid is between one centimeter and eight centimeters.

3. The method of claim 1 in which the countercurrently flowing portion of the liquid moves at comparatively low velocity in the neighborhood of the relatively quiescent portion of the liquid and at comparatively high velocity in the neighborhood of its point of supply to the filaments.

4. The method of claim 1 in which the countercurrent liquid flows downwardly from its point of supply to the filaments along a confined path comprising a portion spaced from the relatively quiescent liquid in the neighborhood of the spinneret through which the liquid flows at constant, relatively high velocity and a portion adjacent the relatively quiescent liquid through which the liquid flows at a velocity which decreases progressively until the liquid flows into the relatively quiescent liquid.

5. The method of claim 1 in which excess liquid is stripped off the filaments at a point beyond the point of supply of the countercurrently flowing liquid to the filaments and flows back along the filaments to the countercurrently flowing liquid.

6. The method of claim 1 in which the filaments with-

drawn from the countercurrently flowing liquid are after-stretched.

7. The method of claim 1 in which the countercurrently flowing portion of the liquid flows downwardly from its point of supply along a confined generally vertical path to the relatively quiescent portion of the liquid in the neighborhood of the spinneret and the filaments are advanced from the relatively quiescent portion of the liquid upwardly through said confined path.

8. The method of making regenerated cellulose filaments which comprises extruding viscose containing from 6 to 8% sodium hydroxide and from 7 to 9% cellulose, and having a sodium chloride salt test value of 4 to 8 upwardly in a generally vertical direction through a spinneret into a relatively quiescent aqueous coagulating and regenerating liquid comprising an aqueous solution of 2 to 5% sulfuric acid, 8 to 12% zinc sulfate and an amount of sodium sulfate between 18% and the saturation limit, to form filaments, passing the filaments upwardly from the relatively quiescent liquid in a confined, generally vertical path through a liquid supplied to the filaments at a point spaced from the spinneret and flowing countercurrently to the filaments along the confined path to the relatively quiescent liquid in the neighborhood of the spinneret, said countercurrent liquid comprising at its point of supply to the filaments, an aqueous solution of 8 to 12% sulfuric acid, 8 to 12% zinc sulfate and at least 18% sodium sulfate, said countercurrently flowing liquid moving at a relatively high velocity at the portion of the confined path away from the relatively quiescent liquid and at progressively decreasing velocity at the portion of the confined path adjacent the relatively quiescent liquid, the filaments being in contact with the countercurrently flowing liquid for a time interval between one-third of a second and three seconds.

9. The method of claim 8 in which the distance the filaments travel through the relatively quiescent liquid is between about one centimeter and eight centimeters.

10. The method of claim 8 in which the distance the filaments travel through the countercurrently flowing liquid is between 40 and 90 centimeters.

11. The method of making regenerated cellulose filaments which comprises extruding viscose containing 6.6% sodium hydroxide and 7.8% cellulose, and having a sodium chloride salt test value of about 5, upwardly in a generally vertical direction through a spinneret into a relatively quiescent aqueous coagulating solution of 4% sulfuric acid, 8% zinc sulfate, and 20% sodium sulfate to form filaments, passing the filaments upwardly from the relatively quiescent solution along an inverted funnel-shaped path through a liquid supplied to the path at a point spaced from the spinneret, introducing a coagulating solution comprising 10% sulfuric acid, 8% zinc sulfate, and 20% sodium sulfate at said point and flowing it countercurrently to the filaments along the path toward the spinneret, said countercurrently flowing liquid moving at a relatively high velocity in the uppermost portion of the path and at progressively decreasing velocity through successively lower portions of the path until it reaches a region surrounding the spinneret, the acid content and the velocity of said countercurrent liquid decreasing with movement along the path whereby it becomes the quiescent liquid adjacent the spinneret, the filaments being in contact with the countercurrently flowing liquid for a time interval of approximately 0.7 second.

References Cited in the file of this patent

UNITED STATES PATENTS

1,626,454	Dreaper	Apr. 26, 1927
2,054,852	Dreyfus	Sept. 22, 1936
2,340,377	Graumann et al.	Feb. 1, 1944