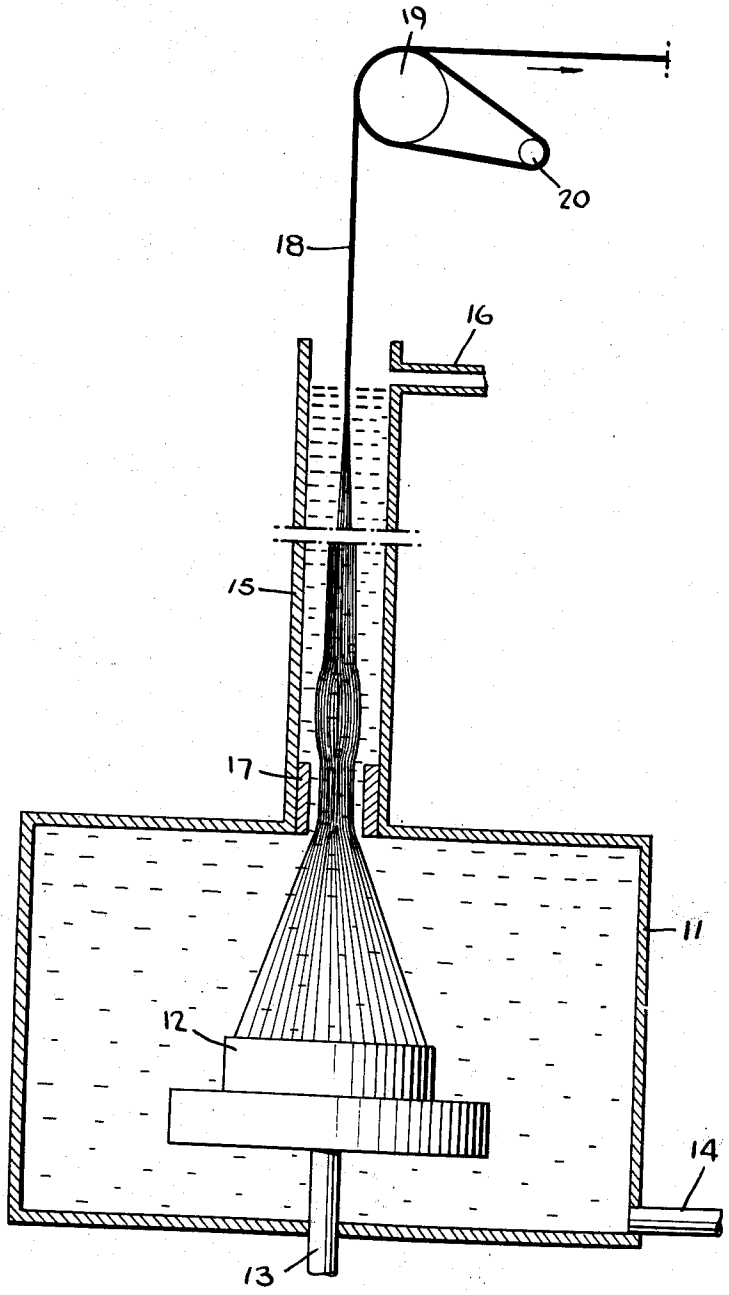
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WET SPINNING COLUMN AND PROCESS

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WET SPINNING COLUMN AND PROCESS

Arnold J. Rosenthal, Whippany, N.J., assignor to Celanese Corporation of America, New York, N.Y., a corporation of Delaware

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The present invention relates to the wet spinning of solutions of filament-forming materials and more particularly to the formation of filaments of cellulose triacetate characterized by superior physical properties.

Synthetic filaments are prepared by forcing a filament-forming material in fluid condition through apertures in a device known as a spinnerette. The filament-forming material may be forced through the spinnerette as a melt, solidifying by cooling; it may be discharged as a solution or dope into an evaporative medium which removes the solvent; or it may be discharged as a solution or dope into a liquid coagulating medium which is miscible with the solvent for the filament-forming material but which is a non-solvent for the filament-forming material itself.

Spinning into a liquid coagulating medium. known as wet spinning, can be effected by continuously passing the dope from the spinnerette into and through a column or tube through which the coagulating medium is continuously flowing. The filaments are pulled through the coagulating medium and generally are drawn down, i.e. the linear speed at which the filaments are withdrawn from the spinning column is greater than the linear speed at which the filament-forming material is discharged through the spinnerette apertures.

It is an object of the present invention to provide a process for wet spinning which permits the formation of filaments of superior physical properties.

It is a further object of the invention to provide a wet spinning process which permits the formation of filaments of high tenacity.

Another object of the invention is to provide cellulose derivative filaments, and particularly cellulose triacetate filaments, of both high tenacity and high elongation.

Yet another object is to provide a spinning column which permits control of the physical properties of filaments formed upon passage therethrough.

Other objects and advantages will become apparent from the following detailed description and claims.

In accordance with the present invention, a dope of filament-forming material is wet spun into a spin bath which flows through a zone, hereinafter called a "high liquid velocity" zone, of the column in the same direction as and at a linear velocity greater than that of the filament-forming material so that the spin bath effects attenuation of the partially coagulated filaments due to the local speed differential. This zone of rapid linear spin bath flow and filament attenuation is followed by a second zone in which the spin bath is flowing much more slowly than the filaments are travelling.

The change in relative flow rates is conveniently effected by an abrupt increase of at least 25% and preferably at least 50% in the cross-sectional area of the spinning column, thereby decreasing the rate at which spin bath flows through the second zone by at least 20% and preferably at least 33%. A similar effect can be achieved, even with a column of uniform diameter, by withdrawing a portion of the spin bath at the end of the high liquid velocity zone so that the linear velocity of the spin bath which is not withdrawn will be reduced in its passage through the second zone.

The novel process of wet spinning filament-forming materials can be effected with dopes of cellulose derivatives such as cellulose acetate, cellulose propionate,

cellulose butyrate, cellulose acetate-propionate, cellulose benzoate, methyl cellulose, ethyl cellulose, benzyl cellulose, and the like. Particularly desirable results are realized when using solutions of cellulose esters containing less than 0.29 free hydroxyl groups per anhydroglucose unit (hereinafter referred to as cellulose triesters) such as cellulose triacetate of acetyl value of at least 59% and preferably at least 61% dissolved to the extent of about 18 to 26% by weight in methylene chloride, advantageously blended with up to about 15% by weight of the total solvent of a lower alkanol such as methanol, ethanol or propanol, of which methanol is preferred. The presence of a small amount of water in the solvent, e.g. about 1% by weight, will not interfere with the process.

For the sake of brevity, the invention will be further described with reference to the spinning of a solution of cellulose triacetate dissolved in a mixture of methylene chloride and methanol. The cellulose triacetate preferably has an intrinsic viscosity in the range of 1.5 to 3, best results being obtained when the intrinsic viscosity is at least about 2. The "intrinsic viscosity" referred to above is that of the regenerated cellulose obtained by complete saponification, without degradation, of the cellulose triacetate. It can be determined according to well-known accepted procedures, using a solution of the regenerated cellulose in cupriethylenediamine.

The cellulose triacetate dope is spun into a coagulant therefor, which is preferably a mixture of methylene chloride and methanol wherein the methylene chloride weight percent is generally below about 50% and preferably within the range of $75\frac{1}{4}-T\pm5$, where T is the temperature of the spin bath in ° C. This temperature preferably ranges from about 20 to 50° C. so that the preferred methylene chloride content of the spin bath ranges from about 20 to 60% by weight.

The spinning column may be disposed horizontally or on an incline but is preferably directed vertically with the dope and spin bath moving upwardly. The linear speed of extrusion of dope can be varied widely, ranging generally from about 5 to 50 meters per minute. The filaments are taken up at a linear speed ranging from about 30 to 3 times the extrusion speed and preferably from about 10 to 5 times the extrusion speed. The highest take-up speed consistent with superior physical properties and freedom from filament discontinuities is preferred since the capacity of the equipment is thereby increased.

The spin bath is fed to the column at such volumetric rate that its linear rate of flow in the high liquid velocity zone ranges from about 40 to 90% and preferably 50 to 80% of the filament take-up speed. Advantageously, the spin bath speed is at least twice and preferably at least three times the extrusion speed. As the only partially coagulated filaments pass through the high liquid velocity zone they are rapidly attenuated by the fast moving spin bath and are speeded up. At the same time they are oriented in a manner which will produce high tenacity upon completion of coagulation, the length of the high speeed zone being selected to give the best physical properties.

The maximum length of the high liquid velocity zone should be about 40 cm. and preferably about 20 cm., corresponding to a minimum length of 60 cm. for the second zone when using a column 1 meter long. On the other hand, the high liquid velocity zone may be very short; for example this zone may be defined by a thin annular diaphragm having almost zero thickness. Preferably, however, the minimum length of the high liquid velocity zone commences from about 2.5 to 15 cm. from the spinnerette face.

Beyond the high liquid velocity zone, the linear rate

of flow of the spin bath is abruptly diminished so that in the second zone the filaments are always moving at a linear speed at least 35 meters per minute greater than that of the spin bath. This creates a hydraulic drag and ensures formation of high tenacity filaments. This abrupt change can be achieved by providing a shoulder in the spinning column which extends perpendicularly to the column axis. Alternatively, the shoulder may be inclined relative to the column axis so as to establish an intermediate transition zone between the high liquid velocity zone and second zone. The length of this intermediate zone of transition should be no more than 10 cm. and preferably no more than 5 cm. to maintain the high tenacity of the filaments.

As noted previously, the linear velocity of filaments varies along the length of the spinning column. The initial and final speeds, i.e. extrusion and take-up speeds are set when starting operation. The linear speed varies inversely with the cross-section of the filaments and thus determination of the filament speed at intermediate locations can be made in several ways by measuring the cross-sectional area of the filaments. This measurement can be made by light transmission since the transmission in a plane perpendicular to the column will depend upon the area of that plane occupied by cellulose triacetate and the area occupied by spin bath. Color may be added substantive either to the spin bath or cellulose triacetate to broaden the differences in light transmission.

Another procedure for measuring the cross-sectional area of the filaments at different locations along the spinning column, and thus of measuring the filament speed, involves terminating extrusion and take-up of filamentary material at the same time, whereby there will be formed a filament rope free at its lower end. The filament rope is permitted to remain in the spin bath for several seconds to harden, and is then removed and dried with little or no shrinkage. The dried filaments are then cut transversely and the cross-sectional area at various locations is measured.

When spinning in a particular column under particular conditions, a change in any one condition to increase the tenacity of the filaments produced will generally be accompanied by a corresponding decrease in the elongation of the filaments. By proceeding in accordance with the present invention, filaments can be produced with the same percentage elongations as filaments produced by other processes but with higher tenacities than conventionally-produced filaments. By selection of preferred conditions, it is possible to produce filaments of both improved tenacity and elongation.

The invention will now be described more fully with reference to the accompanying drawing, schematically showing partly in elevation and partly in section an apparatus suited for practicing the invention.

Referring now more particularly to the drawing, there is shown a spin pot 11 housing a spinerette 12 for the extrusion of dope which is supplied thereto through a conduit 13. The pin pot 11 is provided with an inlet 14 for admission of spin bath, i.e. coagulating liquid. The spin pot 11 communicates directly with a spinning column 15 which is provided near its open top with a liquid run off 16 to carry away spin bath. The column 15 is provided on its inside with an annular insert 17 to define a restricted passageway for flow of spin bath. Dope spun through spinnerette 12 forms a plurality of filaments 18 which pass upwardly through insert 17 and then the balance of column 15 to pass about a positively driven feed roll 19 and idler 20 from whence the filaments can be washed, dried, stretched or subjected to any other aftertreatment.

The following example illustrates the practice of the present invention:

A spinning apparatus was constructed as shown in the drawing with a spinning column length of 1 meter. The face of the spinnerette was positioned 5 cm. below the

spinning column, which for its first 2.5 cm. had a diameter of 1.25 cm. and for the balance of its length had a diameter of 2.5 cm. The spinnerette was provided with 1396 holes each 0.100 mm. in diameter. A spin bath comprising 43 weight percent methylene chloride and 57 weight percent methanol was passed through the pot and column at the rate of 7 liters per minute at a temperature of 32° C.

Cellulose triacetate having an acetyl value of 61.5%, calculated as acetic acid, and an intrinsic viscosity of 2.0 as measured in cupriethylenediamine on cellulose regenerated therefrom, was dissolved in a 91/9 weight mixture of methylene chloride methanol to form a 21.8 weight percent solution. The dope was extruded through the spinnerette at a linear velocity of 10 meters per minute and the feed roll was run at 70 meters per minute. The speed of the spin bath through the 1.25 cm. diameter zone was about 56 meters per minute and its speed through the subsequent zone of greater cross-sectional area was about 14 meters per minute.

The filaments when leaving the restricted zone were travelling at a linear speed of about 56 meters per minute, and were withdrawn from the column at the speed of the feed roll, i.e. 70 meters per minute. Following withdrawal from the column they were dried on a conveyor belt in a relaxed condition. When stressed to break on an Instron tester a sample of 40 single filaments showed an average denier of 3.0 grams per fil, tenacity of 2.37 grams per denier and an elongation of 22.9%.

The foregoing procedure was repeated varying only the internal dimensions of the spinning column. The total column length was maintained at 1 meter. One run was made with the column uniformly 1.25 cm. in diameter. Other runs were made in a column 2.5 cm. in diameter in a first run using no insert and in successive runs using annular inserts which were 2.5, 7.5, 22.5 and 52.5 cm. long. The results are shown in the following table:

Table

Run No.	Length, in cm., of 1.25 cm. diam.	Fiber properties at break	
		Tenacity, g./d.	Elongation, percent
1	None	2.13	25.6
2	2.5	2.37	22.9
3	7.5	2.27	27.1
4	22.5	2.18	29.8
5	52.5	2.13	29.4
6	100	1.83	31.3

By comparing the results in Runs 2 to 5, it can be seen that the column construction can be selected to give maximum tenacity or elongation or intermediate values, as desired. Comparison of Runs 1 and 5 shows that without changing the tenacity the elongation has been increased. Comparing Run 1 with either Run 3 or 4 shows that the novel process produces increases in both tenacity and elongation as compared with spinning through a column of uniform diameter. The novel process permits formation of cellulose triacetate fibers of tenacities above 2.2 grams per denier and elongations above 22% and preferably above 25%. By subsequent drying with controlled or no stretch or shrinkage, cellulose triacetate filaments spun in accordance with the present invention can have their tenacities increased to 2.5 or more grams per denier without reduction in elongation below 20%.

It is to be understood that the foregoing detailed description is merely given by way of illustration and that many variations may be made therein without departing from the spirit of my invention.

Having described my invention, what I desire to secure by Letters Patent is:

1. The process for wet-spinning a solution of a filament-forming material, which comprises extruding said

solution into a spin bath exerting a swelling action thereon to form partially coagulated swollen filamentary material, passing said spin bath and partially coagulated filamentary material through a first zone in which said spin bath travels at a linear speed greater than the extrusion speed of said solution, thereby to attenuate said partially coagulated filamentary material, said first zone commencing at a maximum distance of about 20 cm. from the point of extrusion, passing said spin bath and partially coagulated filamentary material through a second zone in which said spin bath is travelling at a linear speed slower than in said first-named zone and slower than the speed of said filamentary material in said second zone to complete coagulation with the filamentary material under a hydraulic drag due to the greater speed of said filamentary material in said second zone, and withdrawing said filamentary material from said second zone at a speed ranging from about 30 to 3 times the extrusion speed, said spin bath travelling substantially parallel to said filamentary material in said first and second zones.

2. The process set forth in claim 1 wherein the linear speed of said spin bath in said first zone is at least twice the extrusion speed of said solution and in said second zone said filamentary material travels at a linear speed at least 35 meters per minute greater than said spin bath.

3. The process set forth in claim 1 wherein the speed of said spin bath in said second zone is at least 20% slower than in said first-named zone.

4. The process set forth in claim 3 wherein the distance over which the speed of said spin bath slows down by at least 20% is a maximum of about 10 cm.

5. The process for wet-spinning a solution of cellulose triacetate in a solvent comprising methylene chloride, which comprises extruding said solution into a spin bath comprising methylene chloride and a lower alkanol to form partially coagulated swollen cellulose triacetate filamentary material, passing said spin bath and partially coagulated filamentary material through a first zone in which said spin bath travels at a linear speed greater than the extrusion speed of said solution, thereby to attenuate said partially coagulated filamentary material, said first zone commencing at a maximum distance of about 20 cm. from the point of extrusion, passing said spin bath and partially coagulated filamentary material through a second zone in which said spin bath is traveling at a linear speed slower than in said first-named zone and slower than the speed of said filamentary material in said second zone to complete coagulation with the filamentary material under a hydraulic drag due to the greater speed of said filamentary material in said second zone, and withdrawing said filamentary material from said second zone at a speed ranging from about 30 to 3 times the extrusion speed, said spin bath traveling substantially parallel to said filamentary material in said first and second zones.

6. The process set forth in claim 5 wherein the linear speed of said spin bath in said first zone is at least twice the extrusion speed of said solution and in said second zone said filamentary material travels at a linear speed at least 35 meters per minute greater than said spin bath.

7. The process set forth in claim 5 wherein said first zone has a maximum length of about 40 cm.

8. The process set forth in claim 5 wherein the maximum speed of said spin bath in said first zone is about 90% of the speed at which the filamentary material is withdrawn from the second zone.

9. The process for wet-spinning a solution of cellulose triacetate in a solvent comprising methylene chloride, which comprises extruding said solution into a spin bath comprising methylene chloride and a lower alkanol to form partially coagulated swollen cellulose triacetate filamentary material, passing said spin bath and partially coagulated filamentary material through a first zone in which said spin bath travels at a linear speed at least three times greater than the extrusion speed of said solution, thereby to attenuate said partially coagulated filamentary material, said first zone commencing at a maximum distance of about 20 cm. from the point of extrusion, passing said spin bath and partially coagulated filamentary material through a second zone in which said filamentary material is traveling at a linear speed at least 35 meters per minute greater than said spin bath to complete coagulation with the filamentary material under a hydraulic drag due to the greater speed of said filamentary material in said second zone, and withdrawing said filamentary material from said second zone at a speed ranging from about 10 to 5 times the extrusion speed, said spin bath traveling substantially parallel to said filamentary material in said first and second zones.

10. The process set forth in claim 9 wherein the methylene chloride weight percent concentration in said spin bath equals $75\frac{1}{4}-T\pm5$ where T is the temperature of the spin bath in ° C.

11. The process set forth in claim 9, wherein the length of said first-named zone ranges from about 1.25 to 20 cm.

12. The process set forth in claim 9 wherein said first-named zone commences at a distance ranging from about 2.5 to 15 cm. from the point of extrusion.

13. An apparatus for wet-spinning a solution of a filament-forming material, comprising an upwardly directed spinnerette, means for supplying a spinning solution to said spinnerette, a vertical spinning column, a pair of pipe means communicating with the ends of said column to supply to and withdraw a spin bath therefrom, means for positively pumping spin bath to said column, said column being subdivided into a zone of smaller cross-sectional area commencing at a maximum distance of 20 cm. from the face of the spinnerette followed by a zone of greater cross-sectional area more remote from said spinnerette, thereby to cause the spin bath to travel through said zone of smaller area at a higher linear speed than through said zone of greater area, said zone of smaller area having a maximum length of about 40 cm., and means for withdrawing filamentary material from said column.

14. An apparatus as set forth in claim 13 wherein said zone of greater area is at least 50% greater in cross-sectional area than said zone of smaller area.

15. An apparatus as set forth in claim 13 wherein said zone of smaller area has a length ranging from about 1.25 to 20 cm. and commences at a distance ranging from about 2.5 to 15 cm. from the face of the spinnerette.

16. An apparatus as set forth in claim 13 wherein said zone of greater area is at least 60 cm. long.

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