

June 20, 1961

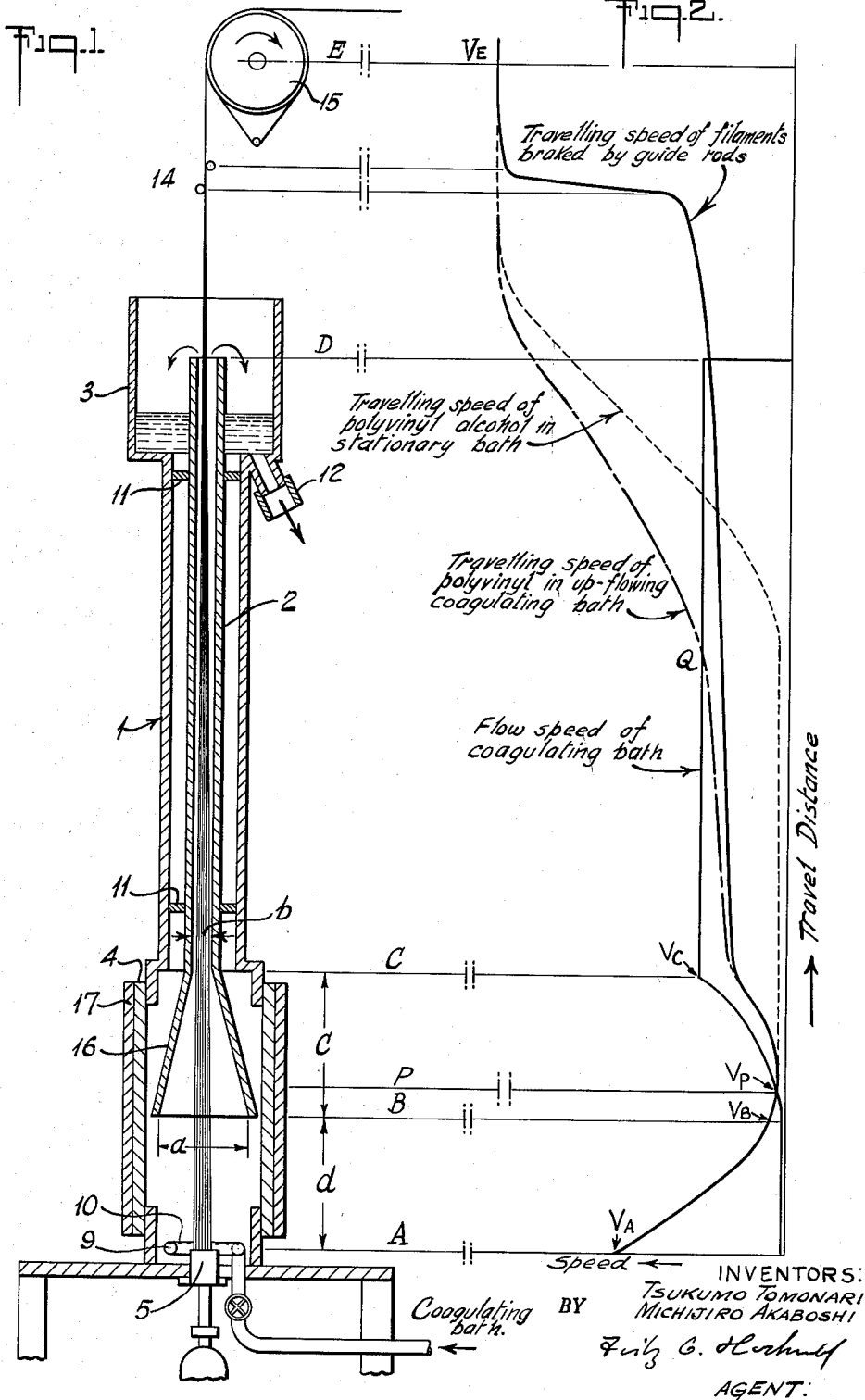
TSUKUMO TOMONARI ET AL

2,988,802

APPARATUS FOR SPINNING POLYVINYL ALCOHOL FIBERS AND PRODUCT

Filed Feb. 10, 1953

2 Sheets-Sheet 1



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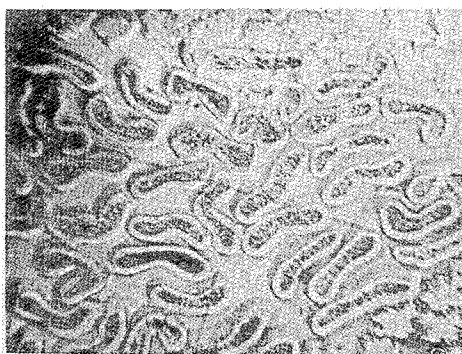
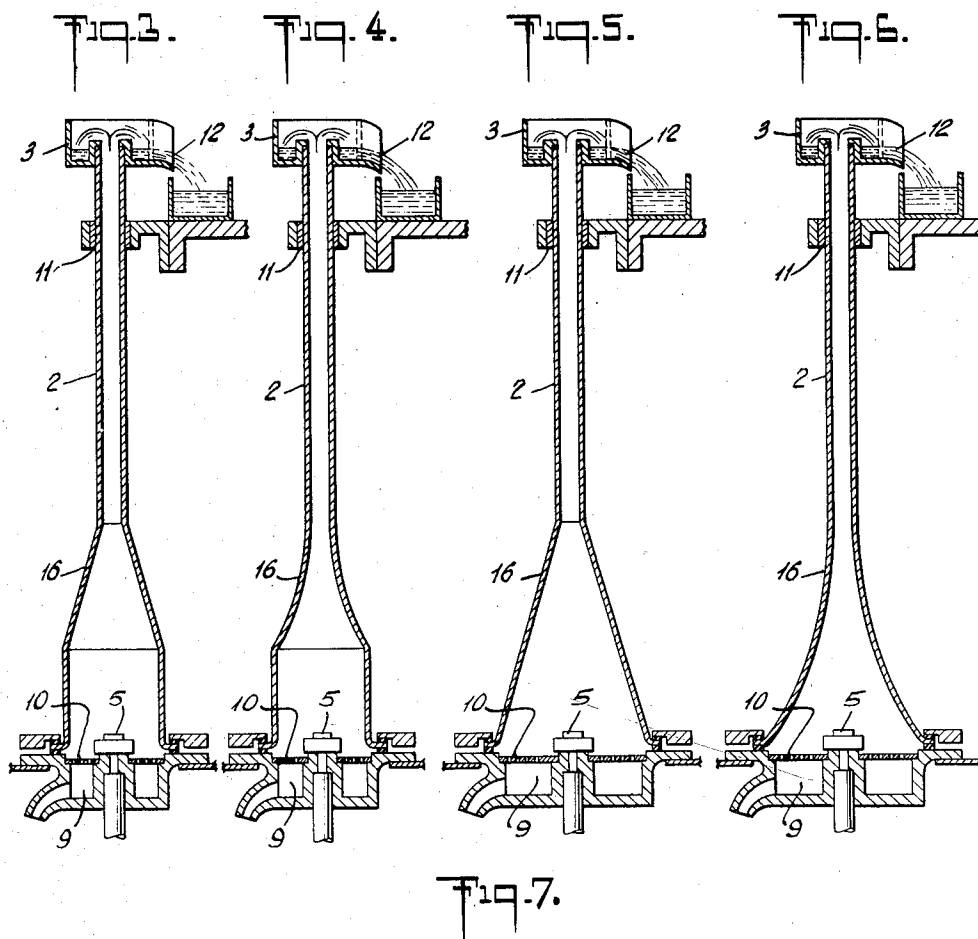
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2 Sheets-Sheet 2



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2,988,802

**APPARATUS FOR SPINNING POLYVINYL
ALCOHOL FIBERS AND PRODUCT**

Tsukumo Tomonari, Osaka, and Michijiro Akaboshi, Kurashiki, Japan; Tatsuko Tomonari and Natsuko Tomonari, heirs of said Tsukumo Tomonari, deceased, assignors, by direct and mesne assignments, of one-fourth to Air Reduction Company, Incorporated, New York, N.Y., a corporation of New York, and three-fourths to Kurashiki Rayon Co., Ltd., Okayama, Japan, a corporation of Japan

Filed Feb. 10, 1953, Ser. No. 336,166

Claims priority, application Japan July 26, 1949

2 Claims. (Cl. 28—82)

The invention relates to the wet spinning of polyvinyl alcohol fibers.

A principal object of the invention is to provide a process for producing polyvinyl alcohol filaments having high tensile strength in the dry as well as in the wet state and high resistance to hot water.

Another object of the invention is to provide a polyvinyl alcohol fiber having the recited characteristics and being suitable as a synthetic fiber for the manufacture of textiles.

Other objects and advantages will be apparent from a consideration of the specification and claims.

The wet spinning process for producing fibers has been particularly developed for the manufacture of cellulose and other fibers from the corresponding solutions of cellulose and cellulose derivatives. The spinning of such solutions is usually based on the coagulation and simultaneous chemical change of the cellulose derivatives dissolved in the solution and stretching of the obtained regenerated fibers to increase their tensile properties. In case of viscose fiber manufacture, for example, the coagulation takes place very rapidly with simultaneous decomposition of the cellulose xanthate to regenerate cellulose in the form of filaments. The solidified filament can be handled safely without damaging the fiber. When using a relatively short dipping length in the coagulating bath and a relatively high spinning speed, good fibers are obtained. The stretching is being applied to the filament during spinning and after spinning to increase the tensile properties.

The process and equipment successfully used for spinning viscose or other cellulose fibers cannot be used for the spinning of polyvinyl alcohol because of its fundamentally different chemical physical, and fiber forming properties; therefore, the conventional spinning methods and devices must be adapted to the specific properties of polyvinyl alcohol in order to spin polyvinyl alcohol fibers which meet the requirements of commercial textiles.

In our copending application, Serial No. 154,872, filed April 8, 1950, now Patent No. 2,642,333, of which this application is a continuation-in-part, we have disclosed and claimed a method of spinning polyvinyl alcohol fibers comprising the steps of extruding a polyvinyl alcohol solution into an up-flowing column of a coagulating liquid having a higher specific gravity than said polyvinyl alcohol solution, imparting to said coagulating column and said polyvinyl alcohol solution a parallel upward direction of flow without turbulence, maintaining said unturbulent parallel flow until the polyvinyl alcohol coagulates to filaments, subsequently reducing the diameter of said column, thereby increasing the rate of flow thereof, and stretching said coagulated filaments by said increased rate of flow and the uplift of the filaments in the specifically heavier column of the coagulating liquid.

In developing our new polyvinyl alcohol spinning process, we had to take into account the following features which are specific to polyvinyl alcohol in aqueous solu-

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tion and distinguish it from other spinning solutions.

(1) During the spinning of an aqueous solution of polyvinyl alcohol, the chemical composition of the polymer is not changed. The physical changes which occur during spinning are coagulation and dehydration which take place very slowly even in a strong coagulating medium. If an aqueous solution of polyvinyl alcohol is extruded into a solution which is capable of coagulating the polyvinyl alcohol, a very thin membrane of coagulated film is formed on the surface of the extruded stream. The coagulating bath diffuses through the membrane in the interior of the stream and slowly coagulates the interior which is still liquid at a time when the membrane is already formed. Simultaneously the water diffuses from the interior of the partly coagulated fiber in the coagulating bath. This partly coagulated fiber consists of a liquid or semi-coagulated core and a very thin outer skin and must be handled very carefully; any disturbance of the fiber as well as any pulling or stretching force should be avoided, as such influences will damage the filament in statu nascendi. Stretch can be applied only after the filament has become strong enough to withstand such forces without damage; for this purpose, the thickness of the surface membrane or skin must be increased until the filaments assume the required strength. Before the filament reaches this state a long contact with the coagulating bath is needed. Although there are means to accelerate the diffusion of the coagulating agent through the surface membrane and such means may somewhat shorten the time interval necessary between the moment when the extruded liquid enters the coagulating bath and the point where stretch can be applied to the filament, they cannot substantially change the characteristic feature of slow coagulation of polyvinyl alcohol solutions.

(2) A second distinctive feature of polyvinyl alcohol fibers is due to the strong cohesive power of the polyvinyl alcohol molecules. The polyvinyl alcohol molecules in the coagulated surface membrane tend to aggregate very rapidly and if a slight pull is applied at the proper time the aggregate is oriented in the direction of the pull; whereas if an aggregate is fully formed in a non-oriented state it becomes difficult to orient the molecules. Therefore, it is necessary to apply a pull at a moment when the molecules are aggregating for the purpose to orient the polyvinyl alcohol molecules. The molecule aggregates are very dense and therefore, those oriented on the surface membrane have the effect of impeding the diffusion of the coagulating agent into the interior of the stream as well as the outward diffusion of the water; consequently, they retard the coagulating progress in the interior part, which results in a filament having a thin oriented surface membrane and a non-oriented core. In order to increase the thickness of the oriented surface skin, a very slight pull is to be applied from the beginning of the coagulation, which pull is to be gradually increased as the coagulation progresses from the outside inwardly. The molecule aggregate forming the skin part of the filament is responsible for the mechanical properties of the filament, and as the oriented skin is developed, the mechanical strength of the filament is increased. The filament with a thin skin obtained at an early stage of the spinning process is not strong enough to withstand a strong external force, for example as applied by solid guide rods; therefore, care has to be taken that the filament is pulled only by the flow of the coagulating bath which has a higher specific gravity than the polyvinyl alcohol solution. The filament is lighter than the coagulation bath and flows up with the bath in the same direction; if the rate of flow of the bath is greater than the floating up speed of the filament, the speed difference exerts a pulling action on the filament. While the filament travels in the bath, coagula-

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tion of the solution progresses. Conforming to the progress of coagulation, the flow speed of the coagulating bath is gradually increased to exert an increasing pull on the filament. By the pulling action the molecules in the surface membrane of the filament are aligned along the direction of the upward flow of the bath and the thickness of the membrane is gradually increased. If the skin part becomes sufficiently thick, then the filament can be stretched without being damaged or broken by an external force such as friction caused by the bath flow or a guide rod. By an adequate strong stretch, the orientation of the molecules is increased and the tensile properties of the filament are improved. During the travel of the filament stream in the bath, the stream or filament is being drawn and the coagulation and dehydration of the polyvinyl alcohol molecules proceed; hereby the diameter of the stream is gradually decreased and the stretching force per unit of cross section must be therefore gradually increased.

In accordance with the properties of polyvinyl alcohol filaments set forth hereinbefore, our process consists in drawing the extruded filamentary polyvinyl alcohol stream and the coagulated filaments in such a way that the drawing (elongation) is larger at the beginning and smaller at the end, whereas the applied stretching force is very slight at the beginning, increases gradually and becomes fairly strong after the coagulation has sufficiently progressed.

(3) The third characteristic feature of polyvinyl alcohol is the limited plasticity of the polyvinyl alcohol aggregates. As the coagulation of polyvinyl alcohol solutions is very slow and the spinning time is very short, a too strong stretching during spinning is apt to destroy the structure of the aggregating filament. In order to improve the tensile strength, it may be necessary to apply an additional stretch to the already sufficiently solidified spun filament, when it can withstand such stronger stretching. But as the polyvinyl alcohol aggregate structure has only limited plastic deformability, it cannot be subjected to such a strong drawing as applied to typical plastic compounds, which would cause unevenness and breakages of the polyvinyl alcohol filaments.

Further characteristic properties of the newly spun polyvinyl alcohol filament are its water sensitivity and solubility, which have to be reduced or eliminated by an after-treatment of the filament. As the invention is concerned substantially with the spinning process proper, the after-treatment of the spun filaments need not be considered here.

For carrying out the spinning process of our invention a suitable polyvinyl alcohol solution and coagulating bath should be used. Among the factors which determine the spinning properties of polyvinyl alcohol solutions, the degree of polymerization (DP) of the polyvinyl alcohol and the concentration of the solution are important. The DP may vary from 1200 to 2500 and the concentration of the aqueous spinning solution from 8% to 20%, increasing with decreasing DP. In special cases as for example for the spinning of very fine denier filaments, the concentration can be reduced below 8% and the DP increased to above 2500. As coagulating bath, an aqueous solution containing one or more inorganic salts such as sodium sulfate, ammonium sulfate, zinc sulfate, is used; the concentration of the salts is preferably close to the saturation point.

The invention will now be described more in detail in connection with the accompanying drawing, in which

FIG. 1 illustrates a suitable apparatus employed for practicing the method of the invention, and

FIG. 2 is a diagram illustrating the flow conditions in the apparatus of FIG. 1.

FIGS. 3 to 6 show modifications of the spinning tube.

FIG. 7 is a photograph of a cross section of staple fiber spun according to the invention (magnification: 390).

The apparatus shown in FIG. 1, comprises a casing 4 and seated therein a smaller tube 1, which ends in the

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receptacle 3. A tube 2 is slidably arranged inside tube 1 and extends into the receptacle 3 and with a trumpet-shaped extension into casing 4. Supports 11 allow of displacing the tube 2 upwardly or downwardly; a shoulder may be provided on the inner wall of the casing 4 to limit the downward movement of the funnel 16.

The wall of the casing 4 can be provided with window openings which are normally closed by the cover 17 and allow of inspecting and adjusting the coagulated filaments.

The casing 4 and tube 2 provide a vertical spinning zone A-D, where the lower part A-B has substantially constant diameter, the middle part B-C has decreasing diameter and the upper part has reduced substantially constant or a very slightly decreasing diameter.

An aqueous solution of polyvinyl alcohol is extruded through small holes of a spinneret 5 into a coagulating bath column. The coagulating bath is fed into the spinning zone through holes 10 of an annular pipe 9 arranged around the spinneret and flows upwardly substantially without turbulence from A to B. The polyvinyl alcohol filaments take form in said unturbulent column and are subsequently drawn by the increasing rate of bath flow in the funnel part 16 and tube 2 until they are taken up by the Godet roller 15. The bath finally flows out from the column top and is withdrawn through the discharge 12. Guide rods 14 may be provided to guide the filament and to adjust the stretch on the filament.

Several factors determine the exact spinning conditions.

(1) The denier of the filament to be spun determines the extrusion amount of the polyvinyl alcohol solution in relation to the spinning speed. The denier of the polyvinyl alcohol filament can be varied in a wide range of about 0.5 denier to about 20 denier.

(2) The extrusion speed (V_A) of the polyvinyl alcohol solution from the spinneret must be higher than the rate of flow of the coagulating bath at A and is determined from the extrusion amount of polyvinyl alcohol solution of a definite concentration and the diameter of the spinneret holes. The speed varies usually from 5 m./min. to 50 m./min. The preferable speed may be in a range of from 10 m./min. to 30 m./min.

The extruded stream of the spinning solution enters the coagulating bath, loses gradually its speed and finally floats up only due to the gravity difference between the filament stream and the coagulating bath. The specific gravity of the polyvinyl alcohol solution is about 1.1, that of the coagulating bath about 1.3. The floating up speed is usually 1.5 m./min. to 3 m./min.

(3) The spinning speed (V_B) is determined by the peripheral speed of the Godet roller and can be changed from about 10 m./min. to about 150 m./min. When the spun filament is taken up by the Godet roller, any resistance applied to the filament results in a drawing of the filament and consequently the speed of the filament is reduced, depending on the extensibility of the filament formed. As such a resistance, the flow resistance of the coagulating bath and the frictional resistance exerted by the guide rods or rollers may be of importance.

(4) The dipping length is the total length of contact of the extruded stream with the coagulating bath. Because of the very slow coagulation of the polyvinyl alcohol solution, the dipping length must be at least 500 mm. and will necessarily be longer for spinning coarse deniers and for spinning at higher spinning speeds. The long dipping length causes a strong flow resistance of the bath to the travelling stream of polyvinyl alcohol and said flow resistance draws the filament and decreases the travelling speed toward the upper part of the lower section of the coagulating column until the traveling speed is reduced almost to the floating up speed of the polyvinyl alcohol stream.

If the coagulating bath does not flow upwardly, the traveling speed of the stream extruded from the spinneret to be taken up by the Godet roller may be schematically illustrated by the dotted line in FIG. 2. The line shows

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that the extruded stream loses its speed in the bath suddenly and after traveling in the bath for 100 to 200 mm. comes to the floating up speed and afterwards increases its speed due to the pull by the Godet roller. At the lower part of the column the pull of the Godet roller may have no influence on the traveling speed of the stream. That means that the stream is floating up freely. The speed change at the upper part of the column, however, is very considerable; that is, the flow resistance of the bath causes a heavy stretching of the filament. At high spinning speeds, the filament would be liable to break during its travel between the top of the column and the Godet roller, and a filament having superior properties could not be obtained. Therefore, it is necessary to reduce the flow resistance due to the long dipping length by causing the coagulating bath to flow up in the direction of the travel of the filament stream or by reducing the traveling speed by guide rods placed beneath the Godet roller.

The flow resistance is proportional to the difference between the flow speed of the coagulating bath and the traveling speed of the filament; it must not be too high in order to avoid injury to the filament. We adjust the flow speed of the bath and the traveling speed of the filament in the upper part of the column so that the speed difference at the end of the coagulation when the filament leaves the bath at D, is not larger than 50%.

(5) The flow of the coagulation bath has a great influence on the spinning of the filaments. The flowing speed in the column changes according to the shape of the column, its position and the amount of liquid, as illustrated in FIG. 2. The flow speed is constant from point A to B, increases gradually and attains again a constant speed at C. The bath flows out from the column at D. The flow of the bath exerts an influence on the traveling polyvinyl alcohol stream, accelerates its traveling rate and changes it to the speed curve shown by the dash-dotted line in FIG. 2. Along this curve the traveling stream is subjected to drawing and stretching and the diameter of the stream decreases. The diameter is also decreased as the coagulation and dehydration progresses.

(6) The distance d of the funnel edge from the spinneret surface is important so far as it determines the moment when the influence of the increasing flow speed of the bath starts. From A to B the extruded stream gradually loses its speed and reaches the lowest speed (V_p). As this flow speed is lower than the traveling rate of the polyvinyl alcohol stream, the bath flow can here not exert a pulling action on the stream. The extruded stream contracts according to the speed decrease and the coagulating bath diffuses into the stream; a very thin coagulated membrane is formed on the surface of the stream, while the interior of the stream remains a semi-coagulated or non-coagulated solution. As the dehydration is very small, the diameter of the stream may increase inversely proportional to the decrease of the speed of the stream.

At the point B where the stream enters the funnel, the stream is pulled by the increasing flow speed of the coagulating bath and the speed of the stream is gradually increased from V_p to V_c . The point (P) where the stream speed is lowest may be located a little higher than the point B, but the difference is small so that the lowest speed V_p may be assumed to be the same as the speed V_B at point B.

At the point P or B the drawing of the stream starts and is caused by the speed difference between the bath and the stream. As previously mentioned, the stretching of the stream at the early stage of coagulation is important and necessary to improve the tensile properties of the produced filament. But a too early start of the stretching would be harmful because such a stretching destroys the coagulation structure whereas a too late start of the stretching would be less efficient because such a stretching contributes little to the orientation of the polyvinyl alcohol molecules which have already aggregated at random. The proper distance d is determined essentially by

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the size of the filament stream but almost independent of the spinning speed of the Godet roller. It may usually vary from 150 mm. to 500 mm. and the traveling speed of the stream at point B when the pulling of the bath flow starts, should be less than 5 m./min., preferably 1.5 to 3 m./min.

(7) The length of the funnel c determines the period of acting on the solidifying polyvinyl alcohol stream by the increasing flow speed. During this travel from B to C, the speed difference between bath and stream gradually increases and consequently the stream is gradually drawn and its diameter gradually decreases. The diameter decreases also due to the dehydration of the polyvinyl alcohol molecules. By the increased drawing, the stretching of the filament stream is increased and the coagulated polyvinyl alcohol molecules are aligned along the fiber axis to improve the tensile properties of the produced filament. At the point C the bath and the filament stream enter into the narrow section of the coagulating column and the speed difference between the bath and the stream attains a maximum.

The flow speed of the coagulating bath at C determines the magnitude of the drawing or stretching applied to the solidifying filament and the shape of the funnel determines the increasing rate of drawing or stretching. The increasing rate and the maximum value of drawing or stretching may be adjusted to the coagulation characteristics of the polyvinyl alcohol solution and they should be neither too big nor too small; the rate of drawing from B to C may be, for instance, about 50 to 150% per second. The appropriate shape of the funnel and the flow speed are easily determined in each practical case, according to the denier of the filament to be spun and to the spinning speed imparted by the Godet roller.

(8) The length of the narrow section of the spinning column determines the continued coagulation and drawing of the filament stream in the coagulating bath column. During the travel from C to D, the flow speed of the bath is constant, e.g. about 5 to 50 m./min., and the traveling speed of the stream increases due to the take up by the Godet roller; therefore, the pulling force exerted by the flow speed of the bath decreases. However, the pulling action by the Godet roller becomes now effective. The stream increases its speed gradually and is taken out of the bath at D with the speed (V_D) and reaches finally at the Godet roller the speed V_E .

Because the spinning speed V_E is usually higher than the flow speed of the bath, the traveling speed of the stream must exceed the flow speed of the bath at a certain point Q; below this point the coagulating bath exerts a pulling action on the stream and above this point the bath exerts a braking action due to the flow resistance against the pull of the stream by the Godet roller. The point Q changes its position according to the relation between spinning speed, flow speed of the bath and dipping length. If the point Q falls below C, the pulling effect of the Godet roller will act on the filament stream at an early stage of the coagulation and may destroy the structure of the solidifying filament stream if the effect is too strong. To avoid this undesirable effect, the length of the section C-D must be extended. However, if the section is too long, the flow resistance of the bath is increased, which may destroy the solidifying stream. The flow resistance should not be too strong, that is, the speed difference between the filament and the bath should be relatively small.

If a mechanical resistance such as guide rods are put between the top of the column and the Godet roller, the travelling speed of the stream in the bath is reduced and the point Q moves toward the point D and may pass this point, in which case the traveling speed at point D becomes lower than the flow speed as illustrated by the solid line in FIG. 2. In such a case, the flow resistance of the bath is decreased but the guide resistance is increased.

During the travel from C to D, the filament is further drawn according to the speed relation and the extensibility of the filament, its diameter is further decreased and the stretching is increased to improve its tensile strength. The rate of drawing in this section is about 10 to 50% per second. By adjusting the dipping length, flow speed of the bath and the position of the guide rods the most suitable conditions may be determined. As stated above, the traveling speed V_D of the filament at D should preferably be about the same as the flow-out speed of the bath and should differ from said flow-out rate by not more than 50%, i.e. $V_D = (1 \pm 0.5) \times \text{flow-out speed of the bath}$.

(9) The filament drawn out from the coagulating bath column at D is taken up by the Godet roller at E. At D and E the filament is already sufficiently coagulated and does not undergo any substantial further coagulation. The distance from D to E is of little importance and may be adjusted to the available space.

To sum up: According to the invention the spinning process is divided in three different stages—free coagulation, drawing and stretching in the bath, and outside of the bath. In the coagulation stage, the speed of the extruded stream is reduced to, or almost to the floating up speed of 1.5 to 3 m./min., at most 5 m./min., and free coagulation without turbulence and without pulling action with stream is obtained. In the drawing stage in the coagulating bath, the stream is drawn by increasing its rate of flow from the lowest speed indicated hereinbefore to a speed corresponding to the flow speed of the bath, exceeding said speed by not more than about 50%. The drawing and consequently the stretching is to be performed over the whole range; it is very slight in the early stages and obtained mainly by increasing the flow speed of the bath, and it is gradually increased in the later stages, where the coagulation has progressed, by the pulling action of the bath flow and sometimes by the flow resistance of the bath. The increase of drawing or stretching should be gradual and a sudden change must be avoided. A spinning column of trumpet shape with gradually decreasing diameter would give the most satisfactory performance; for practical purposes, columns where the upper part is of a constant small diameter as shown in the drawings, are sufficient. The edge of the trumpet can be located closer to A if the diameter of the trumpet edge is big enough and the shape of the trumpet walls gentle enough and if the flow speed of the bath is kept much smaller than the floating up speed of the stream in this zone so as to prevent any turbulent action of the spinning bath in the polyvinyl alcohol stream in the zone of beginning coagulation (see FIGS. 5 and 6).

The drawing of the filament after leaving the coagulating bath can be asserted by means of one or more guide rods or revolving rolls placed before the Godet roller. In this stage, the filament is drawn from the speed near to flow-out speed of the bath to the revolving speed of the Godet roller. The drawing rate may be increased from nearly zero up to five times. When the coagulation is nearly completed, strong stretching and a sudden change are allowable, but also here too strong stretching is to be avoided.

The following examples are given to illustrate the spinning conditions and their relation to the properties of the obtained filament. The dimensions of the funnel used (FIG. 1) were: $a=100$ mm.; $b=25$ mm.; $c=200$ mm.

Example 1

Polyvinyl alcohol having a polymerization degree of 1600 was dissolved in hot water and a spinning solution containing 13.8% by weight of polyvinyl alcohol was prepared.

After filtration and deaeration this solution was extruded at a rate of 156 cc./min. through a spinneret having 1000 holes of 0.08 mm. diameter into a coagulating bath

containing 390 g./l. Na_2SO_4 , the temperature of which was maintained at 45° C. The extrusion speed V_A was 30 m./min. and the take up speed by the Godet roller V_B was 50 m./min. The dipping length in the bath was 1200 mm. The flow speed of the coagulating bath was 15 m./min. Two guide rods were placed before the Godet roller and the speed of the filament at the outlet from the bath was adjusted to about the same speed as the flow speed of the bath.

The spun filament tow was dried at 100° C. and then heated in air at 220° C. for a period of 3 minutes. During drying and heating, the length of the tow was kept constant. After washing and drying a finished tow of 4000 denier composed of 1000 filaments of 4 denier was obtained.

The location of the funnel d was varied, and the results of the influence of the funnel location were as follows:

Location of funnel, d in mm.	100	200	300	400	500
Dry tenacity, g./d.	2.34	2.61	2.94	2.76	2.62
Dry elongation, percent.	33.1	28.1	22.8	21.6	20.4
Wet/Dry tenacity ratio, percent.	60	66	84	87	79
Wet/Dry elongation ratio, percent.	96	99	110	110	112

The results indicate that if the pulling action by the flow of the coagulating bath was too early applied to a not sufficiently coagulated stream of the extruded spinning solution, the tenacity, especially the wet tenacity of the finished filament was lower, and the elongation higher. This shows an insufficient orientation of the molecules. On the other hand, if the pulling action was applied too late, the tenacity and elongation decreased somewhat at the same time, probably due to the injuring influence of the pull by the bath flow or to the stretching applied to the coagulated stream of the spinning solution.

In this example, the highest tensile properties were obtained when the funnel was 300 mm. above the spinneret. If the distance is decreased, then the flowing speed of the bath must be changed. This means that if the pulling action is very slight, it can be applied at an early stage of the coagulation.

Example 2

The spinning conditions employed were the same as in Example 1, with the difference that the location of the funnel was maintained at $d=300$ mm., but its length was varied. Again 4000 denier tow, composed of 1000 filaments, of 4 denier was spun.

The results of the influence of the length c of the funnel were as follows:

Length of the funnel c (mm.)	50	100	150	200	300	400
Dry tenacity, g./d.	2.15	2.56	2.68	2.89	2.94	2.54
Dry elongation, percent.	39.1	29.3	27.5	22.8	20.5	19.8
Wet/Dry tenacity ratio, percent.	57	65	74	84	85	75
Wet/Dry elongation ratio, percent.	95	98	105	110	108	109

The results indicate that if the pulling action of the increasing flow rate of the coagulating bath is applied too rapidly to a not sufficiently coagulated stream of the extruded spinning solution, the tenacity, especially wet tenacity of the finished filament is lower, and the elongation higher. On the other hand, if the pulling action is applied too slowly, the tenacity and elongation decrease.

In this case the most preferable length of the funnel (c) was 300 mm., which is nearly equal to the length of the free coagulation stage.

Example 3

The spinning conditions employed were the same as in Example 1, with the difference that the location of the funnel was secured at $d=400$ mm. and the flow speed of the coagulating bath was varied. A 4000 denier tow composed of 1000 filaments of 4 denier was spun.

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The results of the influence of the slow speed were as follows:

Flow speed of coagulating bath, m./min.....	2	8	16	24
Dry tenacity, g./d.....	2.70	2.97	2.76	2.65
Dry elongation, percent.....	26.6	21.3	21.6	42.7
Wet/Dry tenacity ratio, percent.....	63	88	87	38
Wet/Dry elongation ratio, percent.....	118	103	110	115

From these figures, it is evident that an increase of the flow speed increases the stretching at the earlier stage which results in an increase of the tenacity and a decrease of the elongation of the filament produced. However, if the flow speed is too high, the polyvinyl alcohol stream or thread is too strongly stretched and the orientation of the molecules is disturbed, resulting in low tenacity and high elongation of the spun filament. At a high flow speed, the speed difference between the spinning speed and the speed of the thread at the outlet of the coagulating column is also reduced, which acts in the direction of low tenacity and high elongation under the conditions employed. Optimum properties were obtained at a flow speed of between 8 to 16 meters per minute.

Example 4

The spinning conditions employed were the same as described in Example 1 with the difference that the extrusion speed of the polyvinyl alcohol solution was maintained at 15 m./min., and the location of the funnel was kept at $d=400$ mm., whereas the dipping length was varied. A 2000 denier tow composed of 100 filaments of 2 denier was spun.

Dipping length, mm.....	700	900	1,200	1,500	2,000
Dry tenacity, g./d.....	3.12	3.36	3.31	2.96	2.40
Dry elongation, percent.....	18.4	16.5	16.1	17.9	20.0
Wet/Dry tenacity ratio, percent.....	83	84	75	76	75
Wet/Dry elongation ratio, percent.....	105	121	117	136	115

The figures show that with extension of the dipping length, the stretch exerted on the coagulating thread stream is increased; consequently, the tenacity increases and the elongation decreases. However, for a dipping length longer than 1200 mm. the stretching effect decreases again. This means that stretch applied too late is less effective.

Example 5

The conditions employed were the same as in Example 1 with the difference that the spinning speed was varied. The location of the funnel was maintained at 400 mm. A 1500 denier tow composed of 1000 filaments of 1.5 denier was spun.

Spinning speed, m./min.....	30	50	55	60	70
Dry tenacity, g./d.....	3.39	3.64	3.26	2.61	2.38
Dry elongation, percent.....	16.7	16.6	15.6	14.5	15.3
Wet/Dry tenacity ratio, percent.....	81	84	91	91	83
Wet/Dry elongation ratio, percent.....	106	98	109	115	129

The higher the spinning speed, the larger is the stretching at the later stage of the spinning, which increases the tenacity. But too high speed spinning is apt to destroy the structure of the solidifying thread stream and to decrease the tenacity and elongation. It is to be noted that for higher spinning speeds, larger amounts of the spinning solution must be extruded and a larger degree of drawing between B and E is to be applied, and that such conditions are undesirable for obtaining the stretching effect. However, higher spinning speeds can be employed by properly adjusting the dipping length, the flow speed of the coagulating bath and the funnel distance and dimensions.

Example 6

The conditions employed were the same as in Example 1 with the difference that the dipping length and the flow of the coagulating bath were varied corresponding to the spinning speed. The location of the funnel was kept at $d=400$ mm. and a 2000 denier tow composed of

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1000 filaments of 2.0 denier was spun. Some suitable conditions are shown as follows:

Spinning speed, m./min.....	30	50	70	100
Dipping length, mm.....	700	1,000	1,400	1,800
Flow speed, m./min.....	10	15	20	30
Dry tenacity, g./d.....	3.61	3.55	3.16	2.71
Dry elongation, percent.....	17.2	17.8	16.3	18.5
Wet/Dry tenacity ratio, percent.....	86	84	85	82
Wet/Dry elongation ratio, percent.....	95	96	110	115

The example shows that the ratio of spinning speed to flow speed should be at least 3 and preferably greater. By strictly adjusting the spinning conditions, the properties of the finished filament may be further improved and it can be spun at higher spinning speeds.

Example 7

The conditions employed were the same as in Example 1 with the difference that the extruded amount of the spinning solution, the dipping length, the location and length of the funnel and the flow speed were changed. Tows of different size were spun at a spinning speed of 50 m./min.

Denier of single filament.....	1.0	2.0	4.0	7.0
Dipping length, A-D in mm.....	800	1,000	1,400	1,800
Extrusion speed, m./min.....	7.5	15	30	52
Flow speed of spinning bath, m./min.....	10	12	16	18
Location of funnel d = mm.....	200	250	300	400
Time to travel A-B in sec.....	4	4.5	5	6
Length of funnel.....	200	250	300	400
Time to travel B-C in sec.....	3.4	4	4.5	5.5
Time to travel C-D in sec.....	3.6	4	5.5	6.2
Rate of drawing B-C in percent sec.....	88	80	74	68
Rate of drawing near D in percent sec.....	20	20	20	20
Dry tenacity, g./d.....	3.64	3.55	3.00	2.63
Dry elongation, percent.....	16.6	17.8	19.8	24.3
Wet/Dry tenacity ratio, percent.....	86	84	83	80
Wet/Dry elongation ratio, percent.....	98	96	100	110

The results show that with increasing denier the tenacity decreases and elongation increases, which may be an indication that the stretch applied to the larger denier is insufficient. However, even if larger denier filaments are stretched more strongly, the tenacity does not increase to the high value of the finer denier. The reason for this is that the coagulation of the spinning solution occurs very slowly, that the coagulated polyvinyl alcohol is readily orientated by a slight pulling and the oriented structure retards the progress of coagulation, so that the proportion of the oriented skin layer to the total area of the cross section of the filament will be smaller for higher denier filaments which causes the decrease of tenacity.

The examples show the general influence of funnel location, flow speed, and dipping length on the tensile properties of the filament obtained in the spinning of filaments of different deniers at different spinning speeds. By properly adjusting the conditions, polyvinyl alcohol filaments of very fine denier (0.5) or very coarse denier (20) having excellent superior properties, can be produced at a high spinning speed.

Additional stretch can be applied by providing one or more stretch rollers behind the Godet roller, whereby the speed difference between the Godet roller and the stretch rollers determines the rate of drawing. The additional stretch (second stretch) may be applied to the filaments in air or in a bath. As such a bath, an aqueous solution containing inorganic salts may be used in order to induce a limited, but prevent an excessive, swelling of the filament. The concentration and the temperature of said bath may be varied. Usually a solution of sodium sulfate or ammonium sulfate is employed, having a concentration of more than 200 g./l., and the temperature is maintained above 60° C. At too low concentrations and too high temperatures, the filaments may be softened to such an extent as to be broken by strong stretching. On the other hand, at high concentrations and low temperatures, the filaments are difficult to draw. By strong stretching a stress is induced in the orientated structure which results in crimping when the dried fibers are cut to staples and heated for a short time to temperatures of 140 to 225° C.

If the filaments have been already drawn in the preceding stage, they cannot withstand too strong a drawing or stretching in the second stage, which may destroy their structure. The rate of the second drawing should be limited to less than five times, preferably to less than two times their length. This second drawing may be applied in one or more steps which can be carried on in air and/or in a bath.

The following examples illustrate the influence of the second stretching on the properties of the finished filaments.

Example 8

A 14.0% aqueous solution of polyvinyl alcohol having a polymerization degree of 1600 was prepared and after filtration and deaeration extruded through a spinneret having 1000 holes of 0.08 mm. diameter into a column of a coagulating bath containing 400 g./l. of sodium sulfate and having a temperature of 45 to 47° C. The dipping length was 1250 mm. and the flow conditions of the coagulating bath were appropriately adjusted in accordance with the above examples. The extruded solution stream traveled upwardly in the bath, passed over guide rods, was taken up by the Godet roller at different spinning speeds and led over a second stretch roller, the speed of which was 50 m./min. From the speed of the second stretch roller and the speed of the Godet roller, the drawing rate in the second stretching step is calculated.

The filament tow was then dried at a temperature below 160 C. and then heated in air at 220° C. for 3 minutes. During drying and heating, the length of the tow was kept constant. After washing and drying, a finished filament tow of 3000 denier composed of 1000 filaments of 3 denier was produced.

The tensile properties of the filament produced are illustrated in the following table:

Spinning speed of the Godet roller, m./min.	50	42	33	28	21
Speed of the second stretch roller, m./min.	50	50	50	50	50
Rate of drawing or stretch, percent	0	20	50	80	140
Dry tenacity, g./d.	3.05	3.60	3.50	3.20	2.60
Dry elongation, percent	18.6	19.8	18.2	18.8	19.0
Wet/Dry tenacity ratio, percent	86	88	88	86	86
Wet/Dry elongation ratio, percent	109	106	105	109	112

The results show that a second stretching of between 20% to 50% gives the most desirable effect and that a higher second stretching is less effective.

Example 9

The conditions employed were the same as in Example 8 and the spun tow was stretched to 46% by the second stretch rollers and then further stretched to different rates by the third stretch roller. Between the second stretch roller and the third stretch roller, the tow passed for a length of 200 mm. through a bath containing 280 g./l. of sodium sulfate and maintained at a temperature of 90° C. The speed of the third stretch roller was 50 m./min. From the speed of the third roller, the second roller and Godet roller, the drawing rates could be calculated.

The tensile properties of the 3 denier filament obtained are shown as follows:

Spinning speed of the Godet roller, m./min.	34	29	26	23	19
Speed of the second stretch roller, m./min.	50	42	38	34	28
Speed of the third stretch roller, m./min.	50	50	50	50	50
Rate of the second drawing, percent	46	46	46	46	46
Rate of the third drawing, percent	0	20	30	45	80
Dry tenacity, g./d.	3.56	3.90	4.15	3.82	3.71
Dry elongation, percent	19.0	17.0	17.6	16.5	16.5
Wet/Dry tenacity ratio, percent	88	89	89	89	88
Wet/Dry elongation ratio, percent	105	100	98	102	100

In this case, too intensive stretching in the third stretching stage was less effective and this stretching should be kept within certain limits. According to this example, the best conditions to achieve highest tensile strength and to maintain still an adequate elongation were to stretch to an extent of 46% by the second stretch roller and then to an extent of 30% by the third stretch roller. The total stretch of the second and third stretching stage was therefore $46 + 30 \times 1.46 = 89.9\%$. From these experiments, it is evident that the additional drawing applied to the filament after passing the Godet roller should not be too strong, even though it be applied in several stages, whereas the first drawing applied in the spinning column before the take up by the Godet roller should be very extensive, for example, 10 times or 50 times for drawing the slowly floating thread stream at the funnel edge with a speed of about 2 m./min. to the spinning speed of 20 m./min. or 100 m./min. Therefore, it is important to adjust properly the stretch in the first drawing range.

Example 10

Under the same conditions as in Example 9, a filament tow was spun at a spinning speed of the Godet roller of 30 m./min.; the speed of the second stretch roller was 42 m./min. and the speed of the third stretch roller 50 m./min. Between the second stretch roller and the third stretch roller the tow passed through a second bath containing 250 g./l. sodium sulfate and having a temperature of 95° C.

	Percent
Degree of drawing in the spinning column	510
Degree of drawing between guide rod and Godet roller (14 and E in Fig. 1)	170
Degree of drawing in the 2nd drawing	40
Degree of drawing in the 3rd drawing	19
Total degree of 2nd and 3rd drawing	67

The flowing-up speed of the polyvinyl alcohol stream at the funnel edge 13 was about 1.8 m./min. The spinning speed at the exit of the spinning column D was about 11 m./min. The degree of drawing immediately after leaving the spinning column is determined by the equation (see FIG. 2):

$$100 \times \frac{V_E - V_D}{V_D} = 100 \times \frac{30 - 11}{11} = 173\%$$

The tensile properties of the 2 denier filament were as follows:

Dry tenacity, g./d.	4.25
Dry elongation, percent	15.4
Wet/dry tenacity ratio, percent	87
Wet/dry elongation ratio, percent	103

Example 11

An 11.5% aqueous solution of polyvinyl alcohol having a polymerization degree of 1800 was spun as in Example 10, and a tow of 500 denier composed of 1000 filaments of 0.5 denier was produced. The tensile properties of the filament were as follows:

Dry tenacity, g./d.	4.62
Dry elongation, percent	15.4
Wet/dry tenacity ratio, percent	88
Wet/dry elongation ratio, percent	98

As shown in these Examples, 8-11, the tensile strength of the filament can be greatly improved by applying an adequate additional drawing, whereby the elongation remains suitable for textile purposes.

The fibers spun by our method as described in the foregoing examples exhibit a very characteristic cross section as shown in the photomicrogram of FIG. 7. It will be noted that the fiber consists of a very distinct skin layer and a core. The skin layer is highly oriented and very dense whereas the core is unoriented. The dif-

ference between the two parts can readily be distinguished under a microscope. The ratio of the skin and the core part can be measured with good accuracy. Generally we have found that the fibers spun by our method consist of about 25% to 60% skin part and 75% to 40% core part. The ratio depends on a number of factors, such as the denier spun, the rate of drawing, spinning speed, the polymerization degree of the polyvinyl alcohol. This characteristic structure is a result of our spinning process where the orientation of the skin part is achieved slowly and advantage is taken of the specific coagulating characteristics of the polyvinyl alcohol. As pointed out hereinabove, the polyvinyl alcohol solution contacting the coagulating bath forms a thin skin of coagulated membrane on the surface of the extruded fiberstream. This skin is oriented first slowly in the funnel part of the column; in the upper part of the column the size of the skin part is increased and the degree of orientation is also increased.

The gentle and progressively increasing stretching force resulting from the increased speed of flow in the coagulating column orients primarily the surface membrane and cannot orient the liquid or partly coagulated inner core. The stretching force in this stage is produced by the surface friction resulting from the flow differences of the coagulating bath and the traveling filament. This can act only on layers in contact with the bath whereby the coagulated and aggregate forming polyvinyl alcohol micelles on the surface are oriented along the direction of flow. The core can be dehydrated and coagulated in this stage, but cannot be oriented. At the moment when the skin part is strong enough to allow the application of stronger stretching for the filament—by the guide rods, Godet roller and stretch rollers—both the skin and core part are further oriented. However, at this point already a substantial difference exists in the degree of orientation of these two parts. The degree of stretching in the second and third stage of the spinning process must be a limited one. The degree of plastic deformability of the surface skin sets an upper limit to the degree of stretch. If the limit is exceeded it results in injury to the skin layer. The core is, of course, also oriented to a certain degree during the second and third stretching stage but the degree of orientation cannot be equal to that of the skin layer. The afterstretch, however, partly destroys the skin layer, inasmuch as the outer layer of the skin is cracked and does not form a coherent tight skin over the core. This cracking of the skin is of importance as the cracks in the skin allow the penetration of dyestuffs, water vapor, and other processing agents, in the interior of the fiber. The degree of orientation of the skin layer can be estimated from the X-ray diagrams of the fiber.

If a polyvinyl alcohol fiber is spun by coagulation and afterstretched in one operation after the fiber is completely coagulated, such a distinct structure cannot be achieved, and a polyvinyl alcohol fiber spun by a dry-spinning method has an entirely different internal structure. It has been known that viscose fibers also exhibit a certain degree of core and skin structure. However, due to the extremely fast coagulation of the viscose in the spinning bath an orientation must be achieved by stretching and the degree of orientation of the very faint skin portion is only very slightly higher than the orientation of the core part. The difference in the case of viscose can be seen also by the fact that the transition from core to skin is not sharply distinguishable and that special dyestuffs must be used to recognize the two distinct parts in viscose filaments.

Not only is the skin and core structure characteristic for our fibers but the skin part is largely responsible for the superior physical properties of the fibers. The highly oriented and dense skin imparts the high abrasion resistance of the fiber and the ratio of skin to core determines to a large degree the high wet and dry tenacity and

wet and dry elongation ratio. A fiber composed only of skin would have a very high strength but low elongation and high brittleness, whereas a fiber composed entirely of the core part would have poor strength and excessive elongation particularly in the wet state. The proper ratio of skin can be varied in our process and the fibers produced have a wide range of properties suited for a large number of practical applications.

For drying the spun filaments special cautions are to be taken. If the filaments are relaxed in an unstretched stage, they tend to shrink and said shrinkage occurs unevenly. Therefore, the drying of the filaments should follow directly the spinning or the additional drawing in the stretched state. Drawing of the filaments during drying is to be avoided because it may cause uneven stretching. If a drawing is applied, the rate of drawing should be limited to less than about 10%.

Higher temperatures may shorten the time of drying but may cause sticking of the filaments. The temperature of drying should be maintained lower than 160° C. Low temperature and long time drying are preferred for obtaining even drying, especially for making fine crimped fibers.

The degree of drying is an important factor. If the dried filaments contain much moisture, they tend to shrink in the following heating stage and said shrinkage occurs unevenly and is undesirable, especially for the manufacture of crimped fibers. Therefore, the filament should be dried completely or at least to a content of less than 10, preferably less than 4 percent.

The dried filaments as such are not sufficiently water-resistant. They swell in water to some extent at ordinary temperature and dissolve in water at higher temperature, for example above 70° C. To improve the water resistance, the dried filaments are subjected to an aftertreatment, for instance to a heat treatment in a gaseous medium at a temperature of from 140° C. to 225° C. for a certain period. A suitable heat treatment is disclosed in the co-pending patent applications, Serial No. 154,873, filed April 8, 1950, by Tsukumo Tomonari and Shigeki Nomura, and Serial No. 154,874, filed April 8, 1950 by Tsukumo Tomonari, now Patent 2,639,970, issued May 26, 1953.

Example 12

Under the same condition as in Example 10, a filament tow was spun, drawn in air and in a second bath to an extent of 67% and then dried to a moisture content of 5%. The dried tow was cut into staple fibers and thereafter heated in air at a temperature of 220° C. for 3 minutes. During the heating crimps were developed. The crimped fiber was washed, dried, and finished. The finished fiber had fine crimps and showed the following properties:

Denier	2.03
Dry tenacity, g./d	3.96
Dry elongation, percent	14.4
Wet/dry tenacity, percent	85
Wet/dry elongation, percent	104
Number of crimps per inch	32.0

Example 13

Under the same condition as in Example 8, a filament tow was spun and passed from the Godet roller to a second roller and drawn in air by 67%. After having been dried to a moisture content of 3%, the tow was cut into staple fiber and treated as in the above example. The finished fiber had fine crimps and the following properties:

Denier	5.06
Dry tenacity, g./d	2.86
Dry elongation, percent	18.5
Wet/dry tenacity, percent	85
Wet/dry elongation, percent	108
Number of crimps per inch	26.4

As shown in the examples the tensile properties are

not remarkably injured by heat treatment in the relaxed state. While the heat treatment in the stretched state is applied for making high tenacity filaments, the heat treatment in the relaxed state is useful for making crimped filaments.

The filaments thus spun, stretched, dried, and heat-treated are water resistant and shrink in hot water of a temperature of 80 to 95° C. less than 5%. The water resistance and other properties can be further improved by a chemical treatment with aldehydes, organic acids, and the like.

The term "polyvinyl alcohol" fiber as used in the specification and claims is understood to mean not only a fiber spun from pure polyvinyl alcohol but also fibers spun from copolymers of polyvinyl alcohol with other polymerizable compounds such as ethylene, maleic anhydride, acrylonitrile, and the like, provided such copolymers contain at least 80 percent of polyvinyl alcohol. Such copolymers are known in the art and have been proposed for the preparation of textile fibers in the same way as polyvinyl alcohol.

What we claim is:

1. An apparatus for up-spinning polyvinyl alcohol fibers or filaments comprising a chamber for a coagulating liquid, feeding means at the bottom of said chamber provided with a plurality of apertures for injecting coagulating liquid upwardly in the form of a spray of fine parallel streams into said chamber, a spinneret arranged to

delivery a polyvinyl alcohol solution into said chamber into the center of said injected coagulating liquid, a slidable cylindrical tube extending upwardly from said chamber and opening into said chamber by a funnel of gradually increasing diameter, means to hold said cylindrical tube slidably at a predetermined distance from said spinneret, and a Godet roller above said tube to withdraw the filaments formed in said tube.

2. A textile fiber consisting essentially of polyvinyl alcohol and presenting a distinct core and skin part, the core part making up about 40 to 75 percent by weight of the fiber and consisting of a substantially unoriented polyvinyl alcohol structure, the skin part making up the remainder of the fiber and showing in an X-ray diagram a crystalline structure.

References Cited in the file of this patent

UNITED STATES PATENTS

20	827,434	Friedrich	July 31, 1906
	838,758	Thiele	Dec. 18, 1906
	2,169,250	Izard	Aug. 15, 1939
	2,190,265	Hubert et al.	Feb. 13, 1940
	2,255,594	Berndt	Sept. 9, 1941
25	2,610,360	Cline et al.	Sept. 16, 1952
	2,642,333	Tomonari	June 16, 1953
	2,711,559	Lynch et al.	June 28, 1955

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,988,802

June 20, 1961

Tsukumo Tomonari et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 32, for "celluose" read -- cellulose --; column 3, line 52, for "spining" read -- spinning --; column 4, line 29, for "spung" read -- spun --; line 41, for "30./min." read -- 30 m./min. --; column 6, line 36, for "contined" read -- continued --; column 7, line 10, for "at" read -- as --; column 9, first table, column 5, line 2 thereof, for "2.65" read -- 2.64 --; column 9, line 30, for "100" read -- 1000 --; column 11, line 29, for "160 C." read -- 160° C. --; column 16, line 1, for "delivery" read -- deliver --.

Signed and sealed this 14th day of November 1961.

(SEAL)

Attest:

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