

April 30, 1957

G. W. STANTON ET AL

2,790,700

CONTROLLED COAGULATION OF SALT-SPUN POLYACRYLONITRILE

Filed Jan. 27, 1954

3 Sheets-Sheet 1

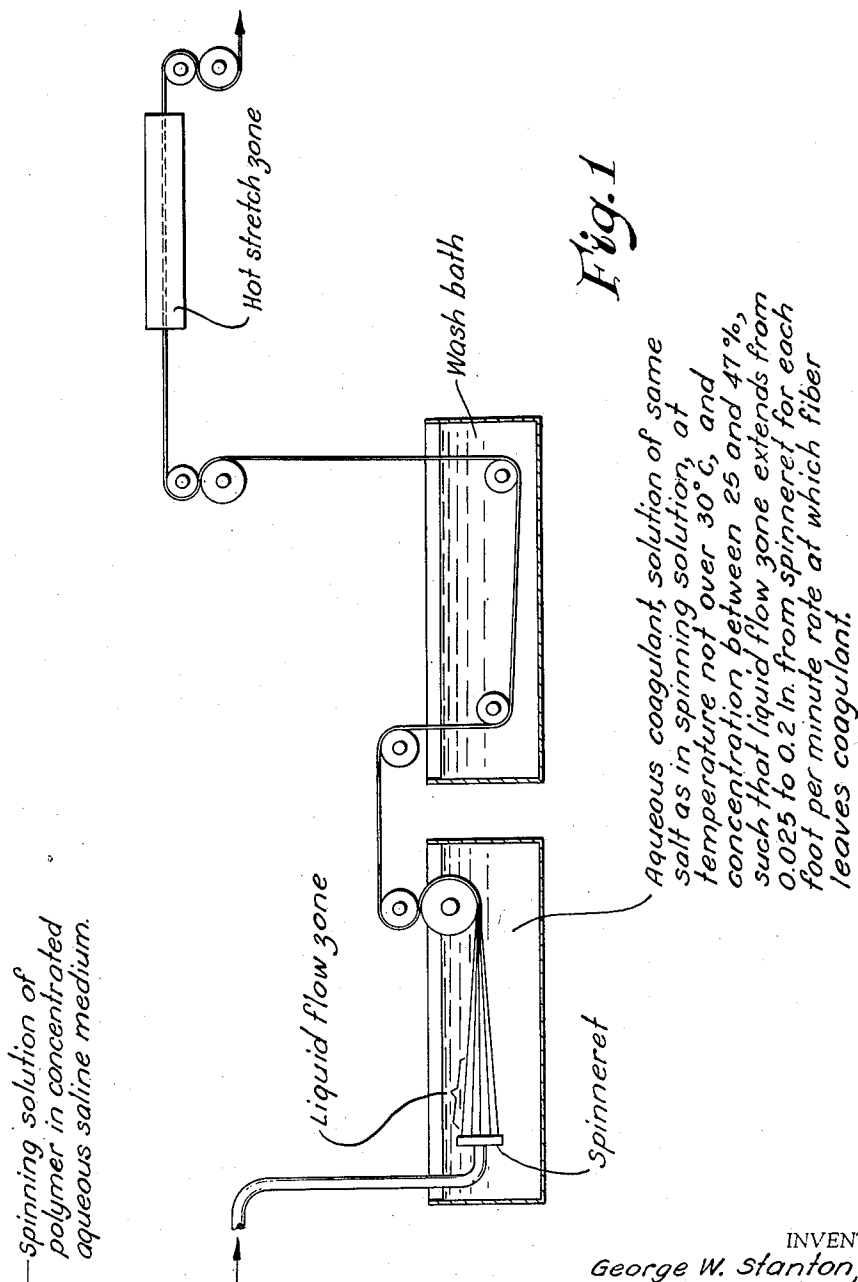


Fig. 1

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3 Sheets-Sheet 2

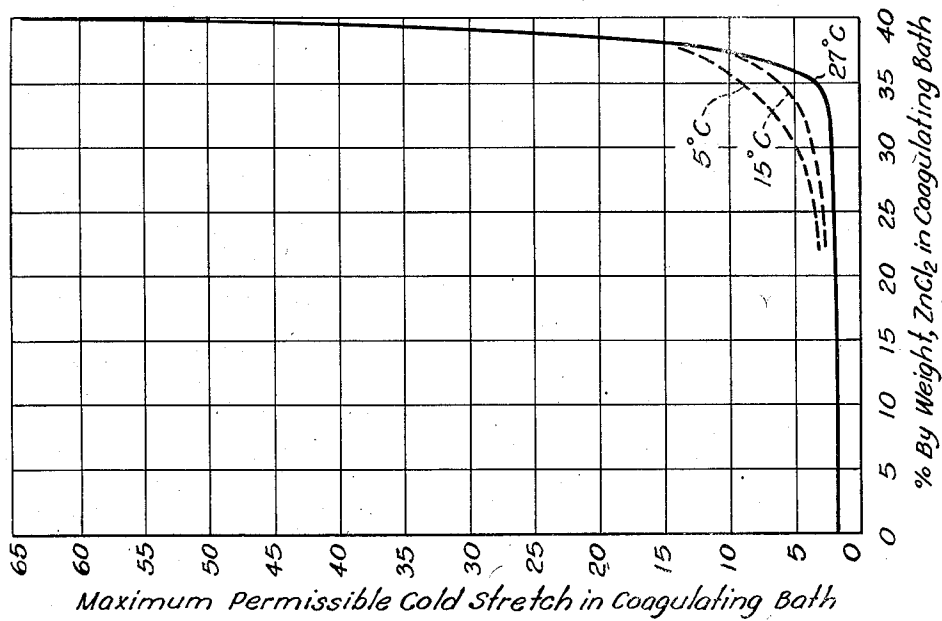


Fig. 3

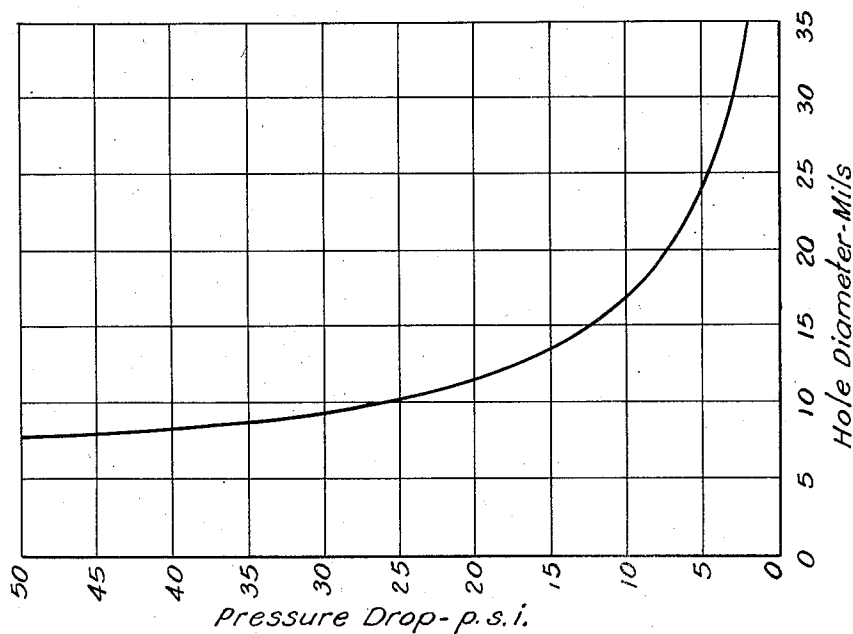


Fig. 2

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3 Sheets-Sheet 3

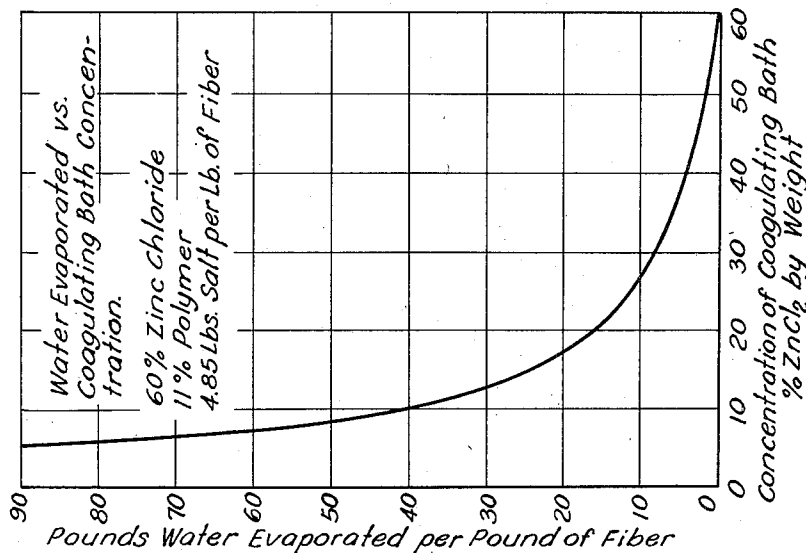


Fig. 5

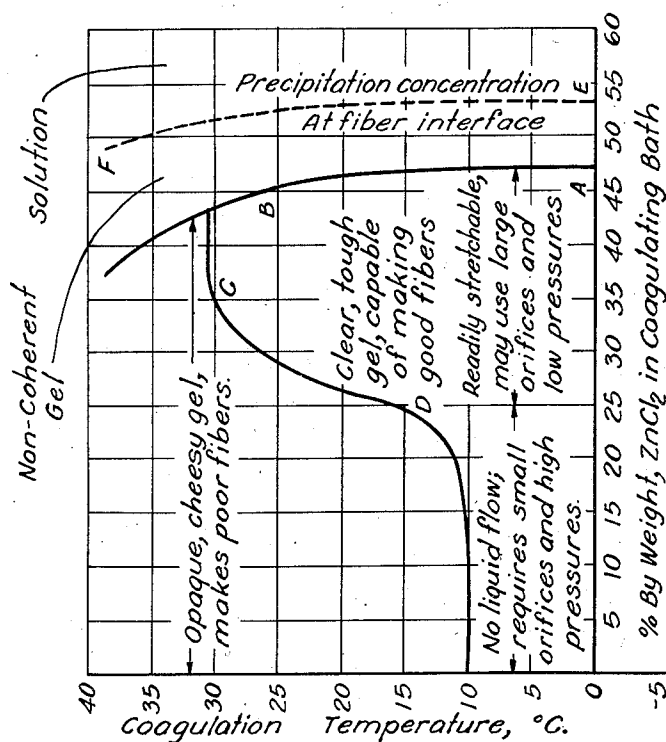


Fig. 4

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CONTROLLED COAGULATION OF SALT-SPUN
POLYACRYLONITRILE

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Application January 27, 1954, Serial No. 406,516

5 Claims. (Cl. 18—54)

This invention relates to the wet spinning of polyacrylonitrile, and of linear fiber-forming copolymers containing at least 85 percent of acrylonitrile in the polymer molecule, from aqueous saline solutions thereof, and is concerned particularly with a method for controlling the rate of coagulation of the spun product so as to assure the production of fibers of consistency high quality.

After the discovery in Germany by Dr. Herbert Rein (see U. S. 2,140,921) that many high polymers, including polyacrylonitrile, can be dissolved in and spun from concentrated aqueous solutions of certain highly hydrated metal salts, such as zinc chloride, it has been reported by other investigators that such salt solutions commonly yield poor fibers when wet spun. The product has been described as brittle, opaque and full of voids. In consequence, much attention has been given to the discovery of organic solvents suitable for spinning polyacrylonitrile by either the wet or the dry spinning procedures.

The use of organic solvents, however, is expensive and results in a fiber having an irregular cross-section, whereas the fibers wet spun from saline solutions are cylindrical. This difference between fibers spun from organic solvents and those spun from aqueous inorganic salts is due to the different behaviors of the two types of solution when brought into contact with a setting medium. Dry spun organic solutions of the polymer merely lose solvent to the evaporative atmosphere, and the fiber-forming material collapses on itself as the solvent is removed. Wet spun organic solutions of the polymer are converted into fibers by extraction of the organic medium from the spun dope by the action of a non-solvent in the coagulating bath. The material in the coagulating bath which is a non-solvent for the polymer must be miscible, however, with the solvent for the polymer. In common practice the coagulant is water, and the polymer solvent is water-miscible. When spun from such organic solutions, the polymer remains hydrophobic. Hence, the freshly coagulated fiber skin acts as a semi-permeable membrane in transferring solvent from the fiber to the bath and allowing essentially no migration of water into the core of the fiber, even when the bath contains a high concentration of solvent. In consequence, the cores of the wet spun fibers from organic solutions shrink and set due to the removal of solvent therefrom and to the resultant radial collapse of the fiber to a denser condition, forming a fiber of irregular cross-section. The effect, then, of both wet and dry spinning of organic solutions of hydrophobic polymers, is primarily one of removing solvent until the concentration of the polymer exceeds the capacity of the remaining solvent to dissolve it. There is no formation of a stretchable gel, and the polymer can only be ren-

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dered plastic by heat in order to be stretched significantly. Because the organic solutions behave in this way, the freshly spun fibers cannot be subjected to any significant amount of cold stretching. Consequently, to make fine fibers from organic solutions of the polymer, one needs spinnerets with very small orifices, and this necessitates high extrusion pressure to move the viscose solutions through the spinnerets.

The present inventors and co-workers have disclosed in U. S. Patents 2,648,646 and 2,648,647 (which were copending with the parent of the present application) that it is possible to obtain good fibers of high acrylonitrile polymers by wet spinning aqueous saline solutions thereof in which the saline constituents are mixed salts, one of which is capable at higher concentrations of dissolving the polymer and the other of which is incapable of dissolving the polymer at any concentration in water. It is shown in those patents that the minimum concentration of saline constituents in water to dissolve high acrylonitrile polymers is 55 percent.

It has been taught by Cresswell and his co-workers, in U. S. Patents 2,558,730-2,558,735, inclusive, and 2,558,781, that useful fibers of polyacrylonitrile may be wet spun from aqueous saline solutions thereof, provided that the coagulating bath is at a temperature not to exceed +10° C. and provided further that the bath be mainly water, with specific mention being made of water alone, aqueous ethanol (to prevent freezing the bath at temperatures down to -15° C.), 0.24 normal hydrochloric acid, and dilute salt (sodium chloride) solutions. The so-coagulated fiber is described as a swollen or gelled article having marked elasticity and toughness. It can be washed free of salt and hot stretched to make strong fibers. The same patents state that when the saline solutions of the polymer are coagulated at temperatures materially above +10° C., the product is a non-transparent, weak gel having little or no ductility. Because of the high viscosity of the saline solution of polymer, the solution is supplied under pressure to the spinneret and its mobility is increased by heating it before it passes through the small spinneret orifices into the cold coagulating bath. The orifices mentioned in U. S. 2,558,730 are of 55 to 90 microns diameter, or from about 0.002 to 0.004 inch. A 40-fiber tow, when given a standard after-treatment, had a denier of 97 (about 2.5 per fil) and a tenacity of 4.1 grams per denier, both being in a very useful range, though the 14 percent elongation indicates the toughness is not as great as may be desired for many uses.

Each of the aforementioned patents relative to wet spinning of saline solutions of polyacrylonitrile is an advance over the prior art, yet none of them teaches a spinning method which is free from certain serious limitations. Thus, as shown by the small orifices required to make fine fibers, and the low temperatures required for coagulation in water and dilute acids, alcohols or salts, it is apparent that low coagulation temperature alone does not assure high rates of production at low extrusion pressures. It has been found, as well, that when fibers are spun from the aforementioned mixed salt brines into such an abrupt coagulant as water, there is obtained a physically non-uniform product. This is due, apparently, to the initial formation of a hard sheath about the still fluid core of the freshly spun fiber, and any stretching to effect a reduction in diameter results in rupturing the fiber.

It is accordingly among the objects of this invention to provide a method for wet spinning aqueous saline solu-

tions of polyacrylonitrile, or of high acrylonitrile copolymers having similar characteristics, whether those solutions contain a single salt or a plurality of salts, whereby controlled coagulation may be obtained consistently: (a) to give clear gels at any desired operating temperature up to 30° C.; (b) to permit the freshly extruded fiber to be cold stretched to effect a reduction in diameter to a desired size smaller than the extrusion orifice; (c) to deliver the fibers in a uniformly gelled state to the washing and hot stretching zones which normally follow coagulation; and (d) to effect substantial economy in the recovery of the saline constituent of the spinning dope. A related object is to provide a method whereby there may be produced consistently fibers which, at any desired denier and tenacity, are capable of high elongation. Other objects may appear hereinafter.

It has now been found that markedly improved fibers may be spun from aqueous salt solutions of polyacrylonitrile, or of high acrylonitrile linear copolymers, containing a single salt or a mixture of solvent and non-solvent salts, when the saline solution medium is extracted gradually and under controlled conditions in the coagulating bath. According to the invention, the saline solution of the polymer is spun first into an aqueous coagulant bath consisting of a solution in water of the same salt or salts as are in the spinning dope, at concentrations controlled within a narrow range but whose absolute values vary with variations in spinning rate, spinneret size, spinning dope concentration, and coagulation temperature. In all cases, the coagulating bath has a concentration of the salt or salts such that the spun fiber can be taken away from the spinneret orifice, without breaking, at a linear rate 4 or more times that at which the spinning dope enters the bath from the spinneret. Unless the freshly spun fiber is coagulated under conditions which would permit such a takeaway rate, no significant dimensional adjustment can be made in the coagulating bath, and, for fine fibers, small orifices are required. Further, unless the fibers initially exhibit liquid-like flow, coagulation is non-uniform, and any after treatment gives non-uniform products. In the case of zinc chloride solutions of polyacrylonitrile, to get this effect, the concentration in the coagulating bath must be at least 25 percent and not to exceed about 47 percent by weight, and for any specific set of operating conditions the optimum operative range of concentrations falls within a narrow bracket within the stated range, as will be illustrated hereinafter. When the strongly saline solution of the polymer is spun into the appropriate lower concentration of the same salt system, complete coagulation is not instantly effected and the fibers are not self-supporting for a short distance, usually more than 1 inch, from the spinneret, as will be described more fully.

Between the orifice and the point at which the fibers are self-supporting or shape-retaining, is a zone in which liquid-like flow of the fluid fibers occurs. In this zone the superficially coagulated fiber has different properties than after it has gelled more completely, and the length of this liquid flow zone can usually be observed ocularly. When the coagulating conditions of the present invention are employed, the zone of liquid flow extends at least 0.025 inch and not over 0.2 inch from the spinneret for each foot per minute linear rate at which the fibers are withdrawn from the coagulating bath. When coagulating conditions are too abrupt, as when water is the coagulant, that zone extends less than 0.025 inch from the spinneret for each foot per minute rate of withdrawal of fibers from the coagulating bath. A liquid zone length much over 8 times the stated minimum accompanies inadequate coagulation. These factors show that the fiber forming material must pass through the liquid flow zone in from 1/4 to 1 second after leaving the orifice, and should be sufficiently gelled by that time to be self-supporting.

The accompanying drawings illustrate various features of the invention, as follows:

Fig. 1 is a flow diagram of a typical spinning operation useful with the invention;

Fig. 2 is a typical curve showing the effect of spinneret size on spinning pressure;

Fig. 3 is a typical curve showing the maximum permissible stretch without rupture in coagulating baths of various concentrations;

Fig. 4 is a plot showing the effects of variations in temperature and concentration in the coagulating bath on the character of the fibers spun in such baths; and,

Fig. 5 is a typical curve showing the amount of water required to be evaporated when recovering the saline constituents from coagulating baths of various concentrations.

As may be seen from the drawings, all other factors being kept constant, the lower the concentration of the coagulating bath, the more difficult it is to make good fibers economically. Thus, when water or weak brines are used for coagulation, low temperatures must be used to get good fibers (Fig. 4); little cold stretch is possible (Fig. 3) and hence, small orifices must be used to make fine fibers; small orifices require high pressures (Fig. 2), and weak brines multiply the cost of salt recovery (Fig. 5). However, at salt concentrations much over 47 percent in the coagulating bath (in the case of zinc chloride systems) there is so little coagulating tendency that the spun dope tends to dissolve or disperse in the bath rather than to form a self-supporting fiber, and the theoretical economies of operating at such high bath concentrations are nullified. The most practical conditions as to spinneret size and coagulant concentration are those found below and to the right, on Figs. 2 and 5, of the points at which a line drawn tangent to the curves has a slope of 45°, i. e., spinneret diameters of 0.015 inch or greater and zinc chloride concentrations in the bath of 25 to 47 percent.

It has thus become apparent that the optimum conditions for making fibers of good quality are those in which the coagulation is effected slowly enough, and the first formed superficial gel is plastic enough, so that the fiber has time to be brought to the dimensions at which it will leave the coagulating bath before it has coagulated completely, or has formed a somewhat rigid sheath of coagulum. The desired slow coagulation is accomplished by reducing the rate of diffusion of the saline constituent from the fiber to the bath, through the use of a strong solution in water of the same saline material. This practice slows the initial rate of coagulation on the surface of the fiber, and permits the diffusion to proceed further into the interior before the surface layers become so low in salt concentration as to be unstretchable under the low takeaway tension. The practice also produces a softer and more plastic gel in the surface layers of the fiber, and these layers can undergo the necessary deformation due to stretching or due to volume changes during leaching without becoming cracked, strained or disproportionately oriented.

When an aqueous saline solution of a fiber-forming polymer or copolymer of acrylonitrile is spun into a coagulating bath, diffusion starts at once, and the interface between the fiber and the bath immediately comes to a concentration which does not vary greatly from the average of the two initial concentrations in the bath and in the spinning dope. In order to form a coherent fiber, it is necessary that this interface be at a low enough concentration so that a superficial gel is formed within a fraction of a second to give enough strength to the fiber so that the spun dope does not sink to the bottom of the bath, or dissolve in the bath, or develop a rough and irregular surface.

For each solution of any polymer or copolymer of acrylonitrile in any aqueous saline medium, there is a minimum concentration of the salt or salts below which the polymer will not remain dissolved at the prevailing temperature, and coagulation must occur in a bath which is at such a concentration that the salt concentration at the

fiber surface must come almost at once to a value below, but not too far below, this precipitation concentration. The precipitation concentration can be determined readily for any of the useful polymers, in any of the useful salt solutions, at any desired operating temperature by a suitable method for determining solubility.

The concentration of the coagulating bath cannot greatly exceed a value conforming to the equation:

Spinning dope concentration—Precipitation concentration=Precipitation concentration—Upper limit of coagulant concentration.

Thus, at 15° C. the precipitation value for polyacrylonitrile spun from aqueous zinc chloride solution is about 53 percent zinc chloride by weight, and a concentration below this value must be attained immediately at the fiber surface when an aqueous zinc chloride solution of polyacrylonitrile is spun into an aqueous coagulant at 15° C. The precipitation value is slightly lower at higher temperatures, as is shown by the line EF in Fig. 4. At 15° C., then, with an aqueous zinc chloride system, the most concentrated coagulant which can be used is determined by the equation:

Spinning dope concentration—53%=53%—upper limit of coagulant concentration.

Assigning the conventional symbol "X" to the unknown upper limit of coagulant concentration, the foregoing equation may be simplified, as follows:

Percent saline concentration in spinning dope + X% = 53%

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This maximum concentration of zinc chloride in the coagulant is shown, for a range of temperatures and for a spinning dope containing polyacrylonitrile in 60 percent aqueous zinc chloride, as curve AB in Fig. 4. It is apparent that the coagulant concentration must be reduced proportionately whenever the concentration of zinc chloride is increased above 60 percent in the spinning dope. It is considered undesirable and impractical to use much more salt in the spinning dope than is necessary to dissolve the polymer, and applicants prefer to use zinc chloride solutions of 58 to 61 percent concentration in the spinning dope.

It is recognized that the line AB of Fig. 4 (or similar lines determined in analogous manner for other systems) defines a limiting bath concentration for producing quality fibers which, after standard finishing operations have high toughness values and uniform orientation. For ease in controlling the bath concentration, and to provide a safety margin for protection against the possible variations in concentration of the bath across a multiple filament tow of simultaneously extruded fibers, it is considered desirable to use a coagulating bath concentration to the left of curve AB (Fig. 4), since the ease of operation away from critical limiting values more than offsets small losses in toughness. The coagulation baths of the present invention should be at concentrations to the right of curve CD, however, as those to the left of CD rigidify the gel so rapidly that poor fibers are obtained, and so little liquid flow is possible that the extruded product can be stretched not over 2.5 times in the bath, often much less than that, without breaking. For reasons given before, it should be possible to vary the speed at which the fiber is taken from the coagulating bath from the linear speed at which it is extruded into the bath to 4 or more times that speed without breaking the fiber. It is not always necessary to withdraw a fiber at 4 or more times the linear rate of extrusion, but, to make good fibers consistently the coagulation rate should be such as to make possible the use of 4 to 1, or greater rates of takeaway.

It is noted that, at coagulation temperatures approaching 30° C., the AB curve and the CD curve of Fig. 4 approach one another. This means that, in the zone near the BC segment of the curve, operating conditions become

more critical and there is less freedom of choice of conditions if good fibers are to be made. In the BC zone, diffusion rates and coagulation rates are much higher than at lower temperatures.

Unlike the coagulated wet-spun organic solutions of acrylonitrile polymers, the coagulated salt-spun fibers behave like permeable membranes, losing salt to the bath and absorbing water therefrom, and the concentration of salt in the coagulating bath controls the rate of this interchange and the quality of the fibers. When coagulation is controlled as here described, the fibers have the property of liquid flow for a short but significant time, and enough reduction may be made in the diameter of the freshly coagulated fibers to make it possible to deliver to the final wash baths and subsequent hot stretching operations a fiber especially suited for the intended use.

The maximum cold stretch obtainable without breaking the gelled fibers in the coagulating bath is shown in Fig. 3 for operations at 27° C., with various concentrations of coagulating baths, using a spinneret 0.015 inch in diameter. The approximate extent to which the curve is affected by changes in coagulation temperature is shown by dotted lines. The following table gives a relationship between the required amount of cold stretch to produce a 3-denier fiber, assuming in each case the washed gelled fiber will be given a 10-to-1 hot stretch, when spinning a solution of polyacrylonitrile in 60 percent zinc chloride solution through various sizes of spinnerets into a coagulating bath consisting of 41 percent zinc chloride solution.

Orifice diameter:	Required cold stretch
0.015 inch -----	10:1
0.0106 inch -----	5:1
0.0075 inch -----	2.5:1
0.00475 inch -----	1:1

The procedure of the invention provides a uniformly gelled fiber by the time the fiber has been drawn down to the desired diameter and washed essentially free of salt. The fiber is then subjected to such typical after-treatment as stretching in steam or hot water to effect orientation and further reduction in diameter. It is found that the properties of the so-oriented fibers, when dried, follow an orderly pattern dependent upon the concentration of the bath in which they were first coagulated and upon the final hot stretch ratio. The term "stretch ratio" employed herein refers to the additional length to which a fiber is stretched for each unit length of the fiber entering the stretching zone. The following typical data illustrate the effects of coagulant concentration and final hot stretch ratio on the ultimate properties of fibers of polyacrylonitrile produced under otherwise identical conditions. The spinning dope was an 11 percent by weight solution of polyacrylonitrile in 60 percent aqueous zinc chloride solution. It had a viscosity of 2000 poises and was spun at the rate of 0.012 pound per orifice per hour through a 1500-hole spinneret, each orifice being 0.015 inch in diameter, into the stated concentration of aqueous zinc chloride coagulant at 20° C. All samples were given a uniform cold stretch in the coagulating bath of 8:1, and, after being washed free of salt without further stretching, were stretched the indicated amount in wet steam. When dried, the so-formed fibers had the properties shown in the following table. The table shows a slight loss in tenacity with increasing coagulating bath concentration at a given steam stretch ratio. However, when higher concentrations are used, it is possible to steam stretch the fibers at a greater ratio, thus ultimately producing a superior product. For example, when fibers were spun into a coagulating bath concentration of 42.5% ZnCl₂, it was not possible to steam stretch without breaks at over 12:1, but with a coagulating bath concentration of 45.5% ZnCl₂, a steam stretch ratio of 16:1 was achieved and a fiber of 4.4 grams per denier tenacity and 29% elongation was produced.

FIBER PROPERTIES vs. COAGULATING BATH CONCENTRATION AND HOT STRETCH RATIOS

Coagulant Concentration, ZnCl ₂	Concen- Percent	Elongation, Percent Steam Stretch Ratio				Tenacity, grams per denier Steam Stretch Ratio					Denier Steam Stretch Ratio				
		8:1	9:1	10:1	11:1	7:1	8:1	9:1	10:1	11:1		8:1	9:1	10:1	11:1
42.4 ¹															
42.5		41	37	33	30		3.0	3.2	3.5	4.1	Range... Average...	3.6-4.5 4.1	3.5-3.9 3.7	3.1-3.2 3.15	2.8-3.1 2.9
42.8		40	36	29	24		3.2	3.5	3.8	4.0					
43.4		45	39	31	26		3.2	3.5	3.7	3.9					
44.0		49	42	34	28	2.9	3.1	3.4	3.7	3.9					
44.3		52	44	36	30	2.7	2.9	3.2	3.5	3.7					
45.5		42	40	39	37		1.7	1.9	2.1	2.7					
45.6 ¹											NOTE.—In any single run, the variation in denier was of the order of 5 percent.				

¹ NOTE.—This concentration of coagulant not usable under these conditions, as the fibers break in the coagulating bath.

The following examples illustrate the practice of the invention:

Example 1

It was desired to make 3-denier fibers, using a spinneret 0.003 inch in diameter. The spinning dope was a 10.5 percent solution by weight of polyacrylonitrile in an aqueous brine consisting of 35.35 percent zinc chloride, 25.95 percent calcium chloride and 38.7 percent water. The coagulant was at 5° C. and consisted of 22 percent zinc chloride, 16 percent calcium chloride and 62 percent water. The zone of liquid flow outside the orifice was about 1 inch long. The coagulated filaments remained in the coagulating bath for 10 seconds and were withdrawn from the bath at a linear rate of about 18 feet per minute, or about 4.5 times the linear extrusion rate. After further washing in more dilute ZnCl₂—CaCl₂ solution and in fresh water, they were stretched 2-fold in wet steam, to about 10 times their original length. After a final water wash they were dried in an air oven and had a denier of 3.0 and a tenacity of 2.43 grams per denier, and were capable of 28 percent elongation.

By way of contrast, some of the same dope was spun through the same spinneret into water at 5° C. The zone of liquid flow was less than 0.1 inch long. The so-coagulated fibers were removed from the bath at about 10 feet per minute, which was the maximum rate possible without rupture, and was only 2.5 times the linear rate of extrusion. After further washing in water, they were essentially salt free, and were stretched as much as possible in wet steam, which was 1.7 times, to a total of about 4.25 times their original length. When washed and dried, these fibers had a denier of 5.5, a tenacity of 1.60 grams per denier and were capable of 21 percent elongation.

Example 2

An 11 percent solution of polyacrylonitrile in 60 percent zinc chloride was spun through a 1500-hole spinneret having 0.015 inch orifices at the rate of 2 pounds of polymer per hour. In order to draw down the fibers enough in the coagulating bath to make possible the production of 1 to 3 denier fibers after a normal 8-to-1 hot stretching operation, it was found that the coagulating bath at 15° C. must be at least 41 percent zinc chloride and not over 45.5 percent zinc chloride solution in water. At lower concentrations of zinc chloride in the coagulant, only coarse fibers could be made, and at higher concentrations fibers could not be produced.

Example 3

A series of runs was made in which polyacrylonitrile solution in aqueous saline media were spun at each of several temperatures into each of several concentrations of the same salt or salts in water. The so-coagulated fibers were given as nearly as possible the same after-treatments, including the maximum permissible cold and hot stretching treatments without rupture. The dried fibers were tested to determine their tenacities, in grams per denier, and their percent elongation under stress to the breaking point. A conventional, but arbitrary, toughness factor was determined for each fiber by means

of the equation: Toughness = $\frac{1}{2}$ tenacity $\times$ percent elongation. The results are tabulated below.

RELATIVE TOUGHNESS FACTOR vs. COAGULANT CONCENTRATION AND TEMPERATURE

Saline Content of Coagulant, Percent	Temperature of Coagulant, °C.						
	-5	0	+5	+10	+15	+20	+25
0 (Water).....	45	40	38	33	25	17	10
20.....	46	40	39	34	33	22	12
43.....	58	63	68	70	74	68	52

It is observed that, while many of the tested conditions have been shown herein not to be ideal, the fibers coagulated in fairly strong solutions of the same salt system as that from which they are spun have a superior combination of tenacity and elongation values. Thus, fibers spun into a 43 percent solution in water of the salt have at least as great a toughness factor when coagulated at 25° C. as those coagulated in water at -5° C., and, at any given temperature of coagulation the order of preference is always the same.

The invention has been illustrated with respect to polyacrylonitrile, but is equally applicable to the fiber forming copolymers of acrylonitrile, and is especially advantageous with those copolymers containing 85 percent or more of acrylonitrile in the polymer molecule, as these most closely resemble the homopolymer in their behavior.

This application is a continuation-in-part of our co-pending application Serial No. 228,755, filed May 28, 1951 now abandoned.

We claim:

1. The method which comprises spinning an aqueous inorganic saline solution of a fiber-forming polymer containing at least 85 percent of acrylonitrile in the polymer molecule through a spinneret into a coagulating bath which is at a temperature not in excess of 30° C. and which consists essentially of a solution in water of the same saline material as is in the solution being spun, the saline concentration of the coagulating bath being in the range from 25 percent to a higher concentration of "X percent" and having such a value in said range that the freshly extruded fiber exhibits a zone of liquid flow extending from the spinneret orifice a distance equal to from 0.025 to 0.2 inch for each foot per minute linear rate at which the fiber is withdrawn continuously from the coagulating bath, thereby permitting the rate of withdrawal of fiber from the bath without breaking to be at least 4 times the linear rate at which the polymer solution is spun into the coagulating bath; washing the so-coagulated fiber to free it of salt, and hot stretching it; the limiting concentration "X percent" being determined from the equation:

$$\frac{\text{Percent saline concentration of spinning dope} + X\%}{2} = 53\%$$

the length of said zone of liquid flow, and the permissible rate of withdrawal of fiber from the coagulating bath, both varying in the same direction as variations

in the coagulating bath concentration in said range from 25 percent to "X percent."

2. The method claimed in claim 1, wherein the polymer is polyacrylonitrile.

3. The method claimed in claim 1, wherein the saline constituent of both the spinning dope and the coagulating bath is predominantly zinc chloride. 5

4. The method claimed in claim 1, wherein the saline constituent in the spinning dope is essentially zinc chloride and the coagulating bath is a solution of zinc chloride in water. 10

5. The method claimed in claim 1, wherein the poly-

mer is polyacrylonitrile, the saline constituent of the solution being spun is zinc chloride, and the coagulating bath is a solution of zinc chloride in water.

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