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PREPARATION OF ACRYLONITRILE POLYMER FIBERS

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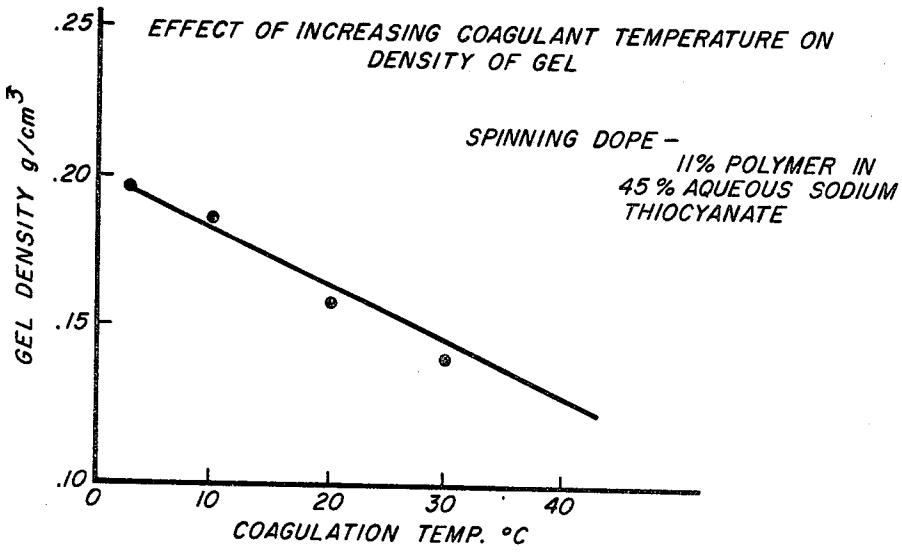


FIG 1

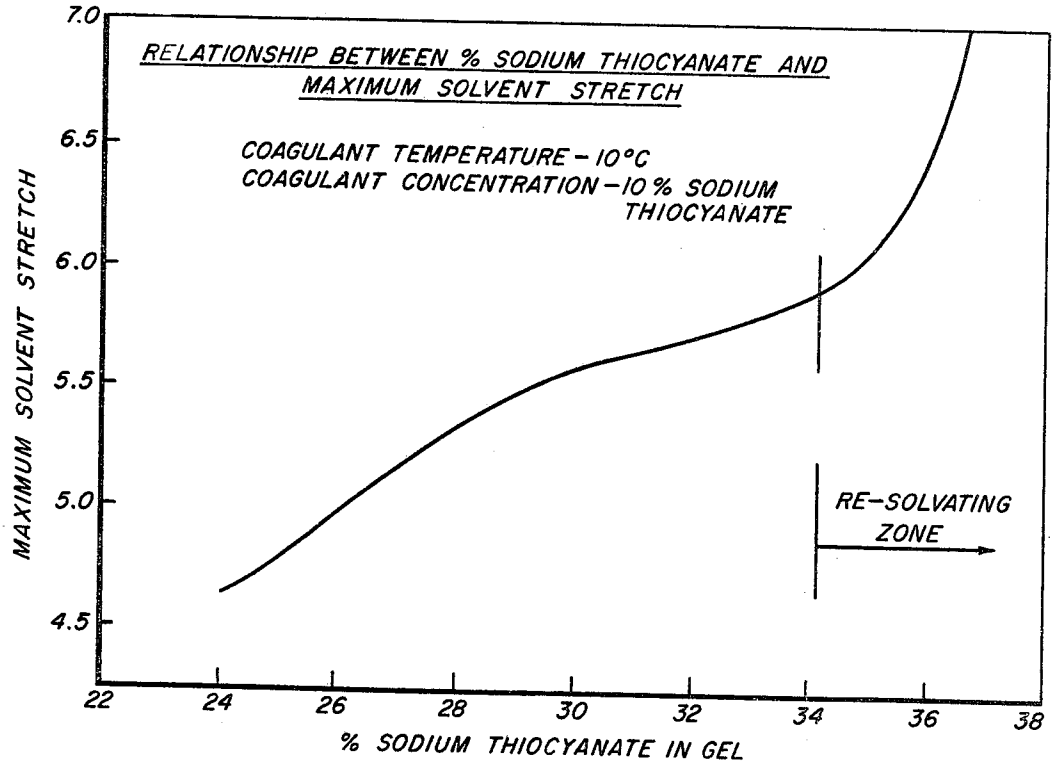


FIG 2

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PREPARATION OF ACRYLONITRILE POLYMER FIBERS

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ABSTRACT OF THE DISCLOSURE

In the process comprising wet-spinning fiber of acrylonitrile polymer from solution thereof in an aqueous saline solvent into an aqueous coagulating medium at a temperature below about 20° C. to form a fiber gel and thereafter washing said gel substantially free of the saline material comprising said solvent and drying said gel to form fiber; the improvement comprising resolvating said fiber gel by treatment thereof with an aqueous saline resolvating solution having a resolvating concentration of saline material which is higher than the concentration in said aqueous coagulating medium and below the concentration in said aqueous saline solvent, whereby the gel, prior to drying, has a lower water-to-polymer ratio and the final fiber has greater strength and higher density than corresponding fiber produced by the identical process without resolvating.

This invention relates to the preparation of filaments from polymers and copolymers of acrylonitrile and, more particularly, it is concerned with an improved method of achieving desirable spinning dope coagulation in wet spinning of fibers of acrylonitrile polymers from solutions comprising less than approximately 15% polymer dissolved in aqueous saline solvents. This invention provide a means for obtaining acrylonitrile polymer fibers from spinning solutions coagulated at temperatures up to 20° C. comprising resolvating the coagulated fiber gel in an aqueous salt solution having a salt concentration higher than the coagulating medium and not high enough to dissolve the gel.

This invention will be understood by reference to the following description and the accompanying drawings in which FIGURE 1 is a graph showing relationship of gel density to coagulant temperature, and FIGURE 2 is a graph showing relationship of maximum stretch of fiber gel to NaSCN concentration in gel.

The spinning of synthetic fibers from solutions containing dissolved acrylonitrile polymers by precipitation of the polymer in filamentary form with an aqueous medium is well-known in the art and has become known as the "wet spinning technique." Many modifications and improvements on original concepts have been proposed and most investigators such as J. P. Knudsen (T.R.J. Jan., 1963) generally agree that a slow rate of coagulation is desirable to the formation of a clear, dense, tough filament gel which is relatively free of micro porous structures. For example, Cresswell, U.S. Patent No. 2,558,730, teaches coagulation in a water or water solvent mixture bath while maintaining the bath temperature below +10° C. The importance of this phenomenon can be appreciated by measuring the density of gel coagulated at different temperatures. When a spinning dope containing 11% polymer dissolved in 45% aqueous sodium thiocyanate (NaCNS) is coagulated by an aqueous solution containing less than 25% NaCNS, the effect of increasing coagulant temperature on the resulting gel (as graphically indicated by FIGURE 1) is one of decreasing gel density. Stanton proposes a technique (U.S.

Patent No. 2,790.700) of controlling the rate of coagulation in $ZnCl_2$ solution by increasing the concentration of salt in the coagulant to greater than 25% and thus permits the use of temperatures up to 30° C. Although such a method allows for considerable economic advantage in reduced refrigeration required to maintain the cold coagulation bath, it has been found that when the inorganic salt is sodium thiocyanate and the concentration of polymer in the spinning solution is less than 15%, gel filaments cannot be formed by the Stanton process or, if formed, have so little gel rigidity as to be commercially inoperable. In addition, large amounts of polymer may be precipitated as a flock or powder rather than in filamentary form. It has been found generally that while an increase in polymer solids level to greater than 15%, desensitizes the effect of the coagulant temperature, the viscosity of saline solutions containing higher than 15% polymer requires excessive heating to impart sufficient fluidity to pass through the spinnerettes. Such heating adversely affects the color of the finished fibers. When sodium thiocyanate is the saline solvent of the process, therefore, it appears that the techniques proposed by Creswell, that is, precipitation of the spinning solution by an aqueous coagulant containing relatively low concentrations of the salt and at temperatures of less than 10° C., have not, prior to the present invention, been significantly improved upon in spite of the considerable amount of investigation conducted on the subject.

It is accordingly among the objects of this invention to provide a method for wet spinning aqueous saline solutions containing 8 to 15% of polymers or copolymers of acrylonitrile whereby clear, tough, uniform cold stretchable gels are obtained after initial coagulation at temperatures up to 20° C., said gels having been resolvated and improved by virtue of having greater strength, higher density and a lower water to polymer ratio. A substantial saving in processing is also realized through lower refrigeration and drying costs.

The invention is based on the discovery that the undesirable gel filaments which are obtained by coagulation temperatures as high as 20° C., as described in U.S. Patent No. 2,558,730, may be treated in a manner which resolvates the gel and thus alters the structure of the gel so that after solvent stretching, washing, hot stretching and dryling, the fiber possesses properties heretofore only obtained by coagulation at lower than 5° C. The invention is further founded on the discovery that said resolvating tends to reduce the amount of water relative to the polymer in the gel prior to hot stretching. Characteristically, the amount of water in the gel substantially higher at increased coagulation temperatures. Thus, a gel coagulated at 20° C. when resolved and washed, has approximately the same water to polymer ratio as a gel coagulated at 0° C. and processed in accordance with the Cresswell teachings. Gel coagulated at 0° C. is even further improved by the process of this invention.

The invention is practiced in its most general form by simply treating an undried filament gel of acrylonitrile polymer with a concentrated aqueous solution of a solvent for the polymer in such way that the gel does not dissolve but is solvated, thus causing the structure of the gel to reform in a more desirable configuration. Said changes in structure may be visually apparent by an improved clarity in the gel but are further reflected as improved properties of the treated gel and finished fibers. The invention is best practiced by spinning fibers from aqueous salt solutions of polymers of at least 70% acrylonitrile and one or more additional ethylenically unsaturated compounds, by coagulating such polymer solutions in water or an aqueous solution containing some of the same salts used to dissolve the polymer to there-

by partially extract such salts, but at a temperature not exceeding 20° C., thereafter resolvating said gel with a second aqueous solution of the same salts at concentrations controlled within a narrow range but whose absolute values are higher than those of the first solution.

In accordance with the present invention, numerous salt solutions are useful as (a) solvent for the polymer, (b) coagulant, and (c) resolvating medium. Illustrative of such salt solutions are those disclosed in Rein, U.S. Patent 2,140,921, issued Dec. 20, 1938, and Stanton, U.S. Patent 2,648,647, issued Aug. 11, 1953.

According to the invention, the concentration of salt in the spinning dope may be any which is capable of dissolving the polymer, but is otherwise not critical. The salt in the coagulating bath can be present in any concentration up to a critical amount beyond which the gel becomes too fluid to be spun without the filaments sticking together. In the case of sodium thiocyanate, it has been found that this critical concentration is approximately 25%, that is, the concentration of NaCNS in the coagulating bath may be varied from 0 to 25% without adversely affecting the beneficial effects of the invention. The gel, so produced, is non-uniform with respect to the degree of coagulation and may have a liquid core but is relatively rigid in that the stretchability of said gel is no more than approximately 4.5 times. When the temperature is above 10° C., the gel is opaque and contains many voids, but so long as the temperature of coagulation is less than 20°° C., such voids can be removed in accordance with this invention by exposing the so-coagulated gels to a second aqueous solution (i.e., the resolvating solution) of the same salts. The second solution must contain a higher and critically controlled concentration of the salt. Concentrations fall within a narrow range and their absolute values vary with the type of salt and the temperature at which the second aqueous treatment is conducted. In the case of sodium thiocyanate, the concentration of the saline solution at room temperature must be between 34% and 38%. It is extremely surprising that this improvement in the gel properties at these high concentrations is obtained since initial coagulation at these concentrations is found to be inoperable. It must be understood that the time of the treatment is a factor also affecting the optimum concentration of the salt in the second aqueous solution. During successful treatment of the gel with the resolvation solution there are changes in the gel properties which usually can be readily observed. As previously noted, the initially coagulated gel appears cloudy or opaque, and has a rigid configuration which resists stretching. During the resolvating process, the gel becomes clear, more fluid and capable of being stretched at room temperature up to 7 or more times its unstretched length. In addition, none of the deleterious behavior, such as flock, etc., are observed. While the resolvating treatment may be successfully applied to initially coagulated gels which are further washed free of all salts, normally for practical considerations, such washing is done after the resolvating and/or solvent stretching step which eliminates the need to wash the gel twice.

It has been stated above that the exact concentration of salt in the resolvating bath cannot be stated within exact limits because of the differences in solvating power between the concentrated aqueous solutions of inorganic (metal) salts, e.g., the chlorides, bromides, iodides, thiocyanates, perchlorates and nitrates, and the effects of temperature at which they are used. In addition, the composition of the polymer gel being treated may dictate, necessarily, a stronger or weaker solvent range above which the gel will dissolve and below which little or no beneficial effects will be noted. In any case, for each polymer gel which has been completely or nearly completely precipitated from its mother solution at a temperature or less than 20° C., there is a range of resolvating solution concentrations such that below it, little or no changes in gel structure are noted, and above it, dissolution of the gel occurs and inoperativeness results. This range can be determined readily for any of the useful acrylonitrile polymers, in any of the useful salt solutions, at any desired operating temperature by determining the stretchability of a gel immediately following the resolvating step. For example, fiber gels were extruded into a bath at 10° C. containing 10% sodium thiocyanate, then washed free of all salt. The gels were then exposed at room temperature to resolvating solutions containing sodium thiocyanate so that the concentration of salt in the gel when equilibrized was varied from 25 to 38%. FIGURE 2 illustrates the effect of solvating power on the stretchability of the gel, indicating a sharp increase in stretchability between 34 and 38%, which is the preferred range in the case of NaSCN. In addition, the clarity of the treated gels was greatly increased. Such techniques may be employed to enable the optimizing of the invention with respect to modifications of its basic concept.

To practice the present invention, it is not necessary to impart a stretch to the gel while it is in the resolvated state; however, the advantages of such stretch orientation are well-known and particular advantage may be made of the sharp increase in stretchability of the resolvated gel by extending or drawing the fiber up to about 7 times its untreated length before washing, thereafter stretching further in water at 70 to 100° C. followed by drying and relaxing the fibers in the conventional manner.

When acrylic fibers are spun from aqueous saline solutions into aqueous coagulating baths, the resulting fiber gel consists of polymer, water which is chemically bound to the polymer, water which is in association with the gel but not chemically bound to the polymer, and a residual salt concentration which must be less than the concentration required to dissolve the polymer. The ratio of these parts to each other is generally a function of the concentration of salt in the spinning solution, the rate at which the spinning is done, the concentration of salt in the coagulating bath and the temperature of the coagulating bath.

It is generally accepted that in wet spinning arcylonitrile polymers, it is most desirable to obtain a wet gel prior to hot stretching or dyeing, which has the lowest water to polymer ratio possible. Such gels, having a greater density, are stronger and less porous than gels with higher water to polymer ratios. It has been found that when gels are formed by coagulating at 20° C., the water to polymer ratio is almost twice that of gel coagulated at 0° C. As originally observed by Cresswell, the gels coagulated at 20° C. are weaker and so porous as to make said gels visually opaque. These poor characteristics are further reflected in the finished fibers which are poorer in strength and flexibility. It is found, however, that by treating gels, coagulated at temperatures up to about 20° C., with a resolvating solution of the present invention, then stretching and washing the gels free of solvent, that the water to polymer ratios are drastically reduced. The treated gels are stronger and far less porous. Although it was found that gels which had been coagulated at 0° C. profit from the resolvating treatment by having a very low water to polymer ratio, the principal advantages are to be gained wherein said treatment follows coagulation at high temperatures, e.g., at 20° C., and allows the preparation of acceptable fibers, whose tensile strength and elongation are vastly improved by resolvating the gel before it is hot stretched and dried. Particularly improved are the loop properties of the fiber. Loop properties are a measure of a fiber's resistance to abrasion. This invention provides, therefore, a means of not only improving the product obtained by the Creswell teachings, but a means which allows a more economical spinning operation by virtue of the drastic reduction in the amount of refrigeration required to maintain the lower temperature of the coagulating bath.

The concentration of salt in the initially coagulated gel is unimportant to the successful practice of the invention so long as a gel is obtained whose properties in terms of strength, etc., allow it to be carried over rolls, etc., and be passed continuously from the coagulating step to the resolvating treatment. It has been found that in the case of NaCNS, this maximum concentration must be less than about 38% on a total solvent basis; however, it is preferable to process gels which have NaSCN concentrations of no more than 30%. The concentration of salt in the case of NaCNS, in the spinning dope may be varied by weight from about 40% (required to dissolve the polymer) to 60% which is the practical limit of solubility in water. As mentioned previously, the coagulating bath may consist solely of water; however in practice some concentration of salt is maintained. In the case of NaCNS, the maximum concentration of salt must be such that gel coagulated by it contains less than 38% NaCNS (solvent basis) and preferably less than 30%. In actual operation at commercial rates of extrusion, the coagulating bath concentration will generally be less than about 25% NaCNS (75% water) since the gel and the bath do no equilibrize.

TABLE I

Example No.	Coag. Temp., ° C.	Treated	Gel Properties: Density, g./cm.³	Gel Properties: Tenacity, g./d.	Total Stretch	Finished Fiber Properties: Straight: Ten., g./d.	Straight: Percent Elongation	Loop: Ten., g./d.	Loop: Percent Elong.
1-A	0	No	0.31	0.76	12×	2.85	45.5	2.50	40.0
1-B	10	No	0.26	0.50	12×	2.47	47.0	1.97	34.5
1-C	20	No	0.18	0.29	12×	1.45	24.0	1.10	9.5

In order that the present invention may be better understood, the following examples are given by way of illustration, but they are not intended to limit the scope of this invention.

EXAMPLE 1

A spin dope was prepared by dissolving 11.2 parts of a copolymer of 89.2% acrylonitrile and 10.8% methyl methacrylate into 88.8 parts of an aqueous solution of 45% sodium thiocyanate. A fiber was prepared in a manner similar to that described in U.S. Patent No. 2,558,730 by passing said dope through a spinnerette into an aqueous bath, maintained at 0° C. and containing 10% sodium thiocyanate, thus forming a filament gel which was stretched approximately 80% of the maximum breaking stretch, then washed free of residual NaCNS with water. The stretched, washed gel thus formed, was clear and had a tenacity of 0.76 gram per denier and a density of 0.31 gram per cm.³. The washed gel was further stretched in water at 95° C. to a total of 12× the original unstretched length, dried and further relaxed in steam under pressure by 36.2% of its stretched length. The final denier was 6.0.

Additional fibers were spun in the same manner except that the temperature of the coagulating solution was in one case 10° C., and in another case, 20° C. As the temperature of the coagulant increased, the gel became more opaque and cloudy.

It will be noted from the data shown in Table I, that with increasing temperature, there is a significant decrease in the density of the washed gel, a corresponding decrease in the tenacity of the gel and a general degradation of all properties measured on the finished fibers.

The example and data clearly show that the use of coagulant temperatures of 10° C. and higher are deleterious to the spinning of good fibers, other conditions being as described. In other experiments of a similar nature, it was determined that varying the concentration of NaCNS in the coagulant solution between 0% and 20% had no significant effect on the results as described.

The density of the gel is determined as weight per unit volume wherein the volume is obtained by microscopic measurement of the gel diameter.

EXAMPLE 2

This example is intended to demonstrate the beneficial effects of the present invention by comparison with Example 1. Unstretched filament gels were prepared as in Example 1 except that in each case, following the initial coagulation, the gel fibers were passed through a solution containing 36% sodium thiocyanate at room temperature to substantially equilibrize therewith. The opaque and cloudy gels became clear and more stretchable. After stretching each sample 80% of the maximum possible without breaking, the gels were washed with water.

TABLE II

Example No.	Coag. Temp., ° C.	Treated	Gel Properties: Density, g./cm.³	Gel Properties: Tenacity, g./d.	Total Stretch	Finished Fiber Properties: Straight: Ten., g./d.	Straight: Percent Elongation	Loop: Ten., g./d.	Loop: Percent Elong.
2-A	0	Yes	0.40	1.00	12×	2.72	42.5	2.37	34.5
2-B	10	Yes	0.36	0.85	12×	2.77	49.0	2.27	35.0
2-C	20	Yes	0.24	0.64	12×	2.25	35.0	1.92	41.5

It will be observed that from the data in Table II that treatment of the present invention increased the density and strength of each gel sample to the degree that the treated gel which had been coagulated at 20° C., was comparable to untreated gel coagulated at 10° C. The significance of said treatment is further seen by examination of the fiber's properties after hot stretching to 12× of the coagulated length, drying and further relaxing 36% to 6.0 den./filament as in Example 1. Thus, compare, in particular, the improved fiber properties of the treated sample 2-C relative to the untreated sample 1-C.

EXAMPLE 3

The effects of the resolvating treatment on the water content of washed gel is demonstrated in this example.

When the cold, stretched, untreated gels of Example 1 were treated in one case with an aqueous solution containing 28% NaCNS and in another, with an aqueous solution of 35% NaCNS it became evident that the amount of total water in association with the polymer gel after coagulation at 20° C. and treatment with 35% NaCNS was no higher than the amount measured when coagulated at 0° C. and not treated. The water to polymer ratio of untreated 20° C. coagulated gel was found to be significantly higher. The water to polymer data shown in Table III is measured by air-drying a known weight of washed gel and is reporter as the grams of water per gram of dry gel. It is important to note that while some improvement in ratio can be expected from a treatment with 28% NaCNS solution, a major effect is obtained at the 35% NaCNS level and is, in fact, required when the gel is coagulated at 20° C. in order to obtain

the gel properties previously obtained by coagulation at 0° C.

TABLE III.—WATER TO POLYMER RATIO

Example No.	Coag. Temp.,[1] ° C.	Grams Water/Gram Dry Gel		
		No Treatment	28% NaCNS Treatment	35% NaCNS Treatment
1-A	0	3.17	2.34	1.63
1-B	10	3.77	3.00	1.94
1-C	20	5.25	4.65	3.16

[1] 10% NaCNS.

We claim:

1. In the process comprising wet-spinning fiber of acrylonitrile polymer from solution thereof in an aqueous saline solvent into an aqueous coagulating medium at a temperature below about 20° C. to form a fiber gel and thereafter washing said gel substantially free of the saline material comprising said solvent and drying said gel to form fiber; the improvement comprising resolvating said fiber gel by treatment thereof with an aqueous saline resolvating solution having a resolvating concentration of saline material which is higher than the concentration in said aqueous coagulating medium and below the concentration in said aqueous saline solvent.

2. The process of claim 1 wherein the aqueous coagulating medium is maintained at a temperature of 10–20° C.

3. The process of claim 1 wherein the aqueous coagulating medium contains less than 25% sodium thiocyanate.

4. The process of claim 1 wherein the resolvating solution is maintained at room temperature.

5. The process of claim 3 wherein the resolvating solution contains sodium thiocyanate.

6. The process of claim 5 including stretching the resolvated gel up to about 7 times its unstretched length.

7. The process of claim 6 wherein said resolvated gel contains 25–38% sodium thiocyanate.

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