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SPINNING OF POLYACRYLONITRILE FILAMENTS

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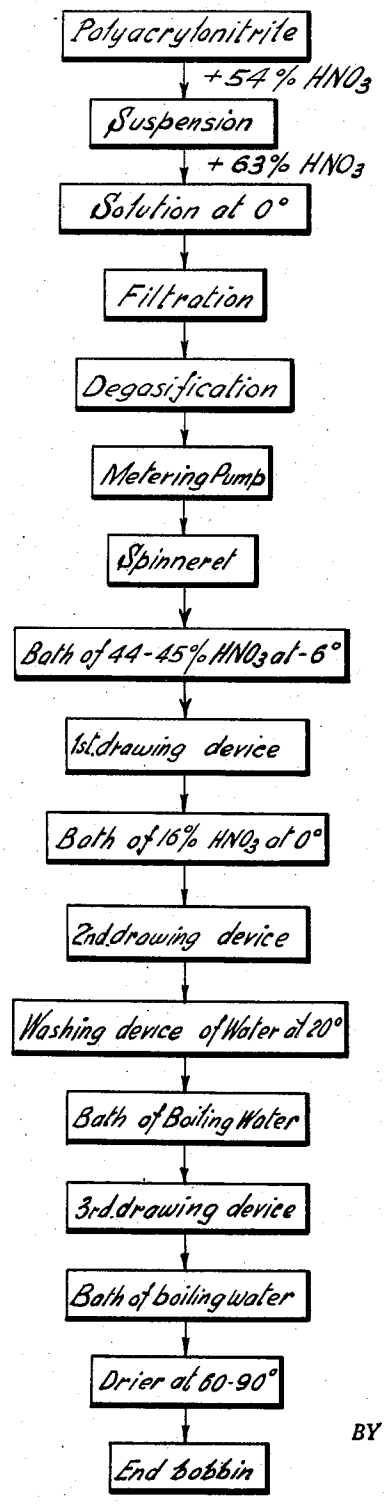

INVENTOR.
PAUL HALBIG
BY Fritz G. Hochwald
AGENT

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SPINNING OF POLYACRYLONITRILE FILAMENTS

Paul Halbig, Fribourg, Switzerland

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3 Claims. (Cl. 18—54)

The invention relates to the spinning of polyacrylonitrile fibers.

In my copending application, Serial No. 311,530, filed September 25, 1952, which is a continuation-in-part of my application Serial No. 236,081, filed July 10, 1951, now abandoned, I have disclosed a method for preparing nitric acid solutions of polyacrylonitrile, which are stable at temperatures below 20° C. for many days without hydrolysis of the nitrile group.

Said method consists in dissolving polyacrylonitrile prepared by polymerization of acrylonitrile in the presence of an organic peroxide, for instance acetyl peroxide, as catalyst, at temperatures of 0 to 80° C. in nitric acid having a concentration of 49 to 68% HNO_3. Preferably, the polyacrylonitrile is first suspended in a 46–54% HNO_3 at temperatures of 0–20° C., and degassed and subsequently dissolved at said temperature by adding higher concentrated nitric acid until the HNO_3 concentration of the solution is about 59%.

Under the recited conditions, the nitric acid is, like dimethylformamide, a true solvent for polyacrylonitrile; in comparison therewith, it is cheaper and has the advantage of allowing processing of the polyacrylonitrile without discoloration.

The nitric acid solutions of polyacrylonitrile are suitable for wet spinning; in such wet spinning procedures, the nitric acid polyacrylonitrile solution is extruded at low temperature into aqueous nitric acid and the formed filaments are washed with nitric acid of gradually decreasing concentration, and finally with water. Subsequently, they are stretched, shrunk, and dried to obtain a fiber suitable for textile purposes. By washing in steps, almost the total amount of the nitric acid introduced as solvent may be recovered in relatively concentrated form and can be concentrated by removal of water to HNO_3 content required for dissolving the polyacrylonitrile. When using a 40% HNO_3 solution as spinning bath, the nitric acid used as solvent is readily recovered in the form of an about 40% acid.

The spinning of unhydrolyzed solutions into a precipitating bath containing more than 30% of HNO_3 presents certain difficulties which are avoided when spinning solutions are used in which part of the polyacrylonitrile has been hydrolyzed to the amide. On the other hand, the use of such partially hydrolyzed solutions has the drawback that it is difficult to maintain a uniform hydrolysis degree; fabrics made of polyacrylonitrile fibers of differing hydrolysis degree show uneven behavior in processing, particularly with respect to dye absorption. A particular drawback of partially hydrolyzed polyacrylonitrile fibers is their reduced weather resistance.

In view of the recited drawbacks of partially hydrolyzed polyacrylonitrile fibers, it is a principal object of

this invention to provide a method of spinning unhydrolyzed nitric acid polyacrylonitrile solutions.

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

The difficulties encountered in spinning unhydrolyzed solutions of polyacrylonitrile in nitric acid are connected with the HNO_3 concentration of the spinning bath. If the spinning bath has a concentration of 30% HNO_3, the spinning of satisfactory fibers is possible only at temperatures around 0° C. If the HNO_3 concentration in the spinning bath is raised to about 40%, the temperature of the bath must be decreased below 0° C. At such low temperatures, the spinning solution tends to gel, which results in further difficulties. The principal difficulty for a technical procedure, however, is due to the fact that the rate of drawing of the filament from the spinning nozzle decreases with increasing concentration of the HNO_3 in the spinning bath. While it is possible to spin into a coagulating bath containing less than 40% of HNO_3 at a rate of feed which is close to the theoretical rate, coagulating baths containing 40% of HNO_3 and more, lower rates of drawing are required. This limitation becomes particularly troublesome if attempts are made to increase the yield of the spinneret, as shown in Table I below.

In said table, V_1 designates the theoretical rate of delivery, in m./min., as calculated from the amount of solution Q (cc./min.) fed by the spinning pump to the spinneret, the number Z of the spinneret holes and the diameter thereof in mm., according to the equation

$$V_1 = \frac{Q \cdot 4}{Z \cdot \pi \cdot D^2}$$

The figures of Table I were obtained with a 10% solution of polyacrylonitrile in 59% HNO_3 and a coagulating bath of 40–43% HNO_3 at a bath temperature of −4 to −7° C. The spinneret was made of chromium-nickel steel and had 10 holes of .2 mm. diameter each. V_2 designates the maximum rate of drawing at which operation was still possible. G defines the rate of drawing in percent of the rate of delivery V_1.

TABLE I

[Coagulating bath 40–43% HNO_3; −4 to −7° C.]

Q	V_1, m.	V_2, m.	G, percent
.4 cc.	1.27	1.20	96
1.6 cc.	5.08	4.00	79
3.2 cc.	10.16	6.20	61
6.4 cc.	20.32	9.50	47

I have found that V_2 can be increased abruptly many times, when, under otherwise unchanged conditions, the concentration of the coagulating bath is increased to 44–46% HNO_3. This is shown in Table II.

TABLE II

[Coagulating bath 44–46% HNO_3; −4 to −7° C.]

Q	V_1, m.	V_2, m.	G, percent
.4 cc.	1.27	>5	>400
1.6 cc.	5.08	>25	>400
3.2 cc.	10.16	>40	>400
6.4 cc.	20.32	>82	>400

The tables show that coagulating baths having a HNO_3 content below 43% HNO_3 allow a maximum rate of drawing only below 100% of the rate of delivery, while on increase of the HNO_3 content in the coagulating bath to above 43%, the rate of drawing can be suddenly increased to several 100%. If the HNO_3 concentration in the coagulating bath exceeds 46%, the spinning operation stops, because the spinning solution leaving the spinneret coagulates too slowly. The increase of the rate of drawing is possible only within the narrow limits of 43–46%, preferably 45±1% HNO_3, in the coagulating bath. I do not have a satisfactory explanation for this phenomenon, but I believe that there may be some kind of connection with the observation that polyacrylonitrile is not soluble below 100° C. in nitric acid weaker than 46% (see Swiss Patent No. 299,374).

With respect to Table II, it may be noted that it is, of course, also possible to spin at a rate of drawing below the maximum rate, for instance at a rate of 150–300%. However, such filaments have, after processing, a hazy and opalescent appearance. This drawback can be obviated by decreasing the temperature of the coagulating bath, but this increases, as set forth above, the risk of gelation of the spinning solution. If, however, the rate of drawing is kept at 400% of the rate of delivery, the filaments remain, at the same temperature of the coagulating bath, clear, even though said temperature may rise by some degrees.

A particular advantage of my process is that the freshly spun polyacrylonitrile filaments can be stretched in the coagulating bath itself; this has not been possible in other methods of spinning polyacrylonitrile filaments from nitric acid solutions, where the obtained filaments could be stretched only after washing at elevated temperatures. Such stretching has not the same favorable effect on the filaments as the cold stretching in the coagulating bath. The stretched filaments obtained according to the invention in the coagulating bath can be, of course, after-stretched after washing, and processed like other polyacrylonitrile fiber to impart thereto specific properties.

The method of the invention may be carried out as follows: The spinning solution is forced by a metering pump through the spinneret submerged in the coagulating bath. The required pressure is, even at high rates of spinning, relatively low, for instance 2–10 kg./cm.^{2}, since even very fine titers may be spun with relatively large holes of the spinneret: for instance, individual titers of .2 denier can be obtained with holes of .10 mm. diameter. The coagulation and solidification of the spinning solution entering the cold coagulating bath proceeds very quickly. Already a few centimeters behind the spinneret, the separate filaments do no longer stick together and may be combined to a bundle which is passed through a first drawing device. Subsequently, the filamentary bundle is washed stepwise with gradually weaker nitric acid, and finally with water. The rate of drawing is adjusted to about 400% of the theoretical rate of delivery from the spinneret, which results in a cold stretching of the filaments. The mechanical devices used may be the same as conventionally used in the wet spinning of viscose.

The coagulating bath is maintained at a temperature of −4 to −7° C. and at a HNO_3 concentration of 43–46%, preferably 45±1%. The temperature of the washing solutions of lower HNO_3 concentration may be higher by a few degrees, and the temperature of the wash water may go up to 20–30° C. The concentration of the HNO_3 in the subsequent washing baths is maintained substantially constant by addition of nitric acid of lower concentration to compensate for the higher concentrated acid introduced from the spinning solution. The recovery of the nitric acid is substantially complete after 4 washing steps, where the first bath contains 43–46%, the second bath 15–20%, the third bath 4–6% and the fourth bath .5 to 2% of HNO_3. The concentration of said bath solutions may be kept constant by passing wash water into the fourth bath and transferring solution from one wash step to the next higher concentrated bath. 43–46% nitric acid is drawn off from the coagulating bath, which nitric acid is concentrated by fractionation and then used again as solvent for the polyacrylonitrile. After complete removal of the nitric acid from the filamentary bundles, the bundles can be processed in the usual manner, for instance by stretching them at high temperatures, shrinking and drying.

The following examples are given to illustrate the method of the invention with reference to the attached flow-sheet indicating the sequence of the various steps. All parts and concentrations are given by weight, unless indicated otherwise.

Example

150 g. of finely powdered polyacrylonitrile having an average molecular weight of 60,000, a density of .4, and a particle size of .01–.10 mm., are stirred at 0° C. into 525 g. of aqueous nitric acid containing 54% of HNO_3. To the thus obtained suspension, 855 g. of aqueous nitric acid containing 63% of HNO_3 are added at an absolute pressure of 20–40 mm. Hg. By stirring at 0° C., the mass is converted to a clear solution within a few minutes. Said solution contains 9.8% of polymer in aqueous nitric acid of 59.5% HNO_3. The gelling temperature of the solution is at about −9 to −12° C. The solution can be stored at temperatures of 0 to −5° C. for at least 250 hours without chemical changes. The viscosity of the solution at 15° C. is 90 P.

The solution is filtered at 0° C. through a filter material consisting of polyvinyl chloride, degassed and forced by a metering pump of acid resistant steel through a spinneret submerged in the coagulating bath, which consists of aqueous 44–45% nitric acid. The temperature of the coagulating bath is adjusted to −5 to −7° C. The obtained filaments are taken up as tow by a drawing device rotating in the spin bath and passed therefrom to a second drawing device which rotates in a bath of aqueous nitric acid of about 0° C. containing about 16% of HNO_3. Both drawing devices consist of a godet wheel which is capable of taking up and giving off the tow. From the drawing device, the tow is passed into a washing device, where it is washed acid-free with water at room temperature. Subsequently, the filamentary bundle is passed through a boiling water bath (stretch bath) to a third drawing device, and hence it is passed through a second boiling water bath (shrink bath) and drier, which is operated with air of 60–90° C., to the end bobbin, where it is wound up with a tension of less than 10 g. per 100 denier.

The seven examples of Table III were carried out in the above described apparatus. The columns of the Table III designate

(*a*) The number of the example;
(*b*) The amount of solution fed by the metering pump to the spinneret in cc./min.;
(*c*) Number and diameter of the spinneret holes,
(*d*) Theoretic rate of delivery V_1 in m./min., calculated from the amount of solution, number and diameter of spinneret holes (see equation in column 2, line 30);
(*e*)–(*i*) Rates of drawing at the five drawing devices. The invention is concerned only with the ratio of the rate of drawing IV, listed in column *g*, to the rate of delivery V_1 given in column *d*;
(*k*) Stretch of the fresh filament in aqueous nitric acid between the admission of the solution through the spinneret (column *d*) and the washing device (column *g*) as percentage of the theoretic rate of delivery V_1;
(*l*) Titer of the finished individual filament in denier;
(*m*) Tensile strength of the individual filament in g./den.;
(*n*) Elongation at break in percent.

TABLE III

(a) No.	(b) cc./min.	(c) Spinneret	(d) I m./min.	(e) II m./min.	(f) III m./min.	(g) IV m./min.	(h) V m./min.	(i) VI m./min.	(k) Stretch in percent	(l) Titer, Denier	(m) Tensile strength, g./Denier	(n) Elongation at break, percent
1	2.6	100/0.15	1.48	1.8	5.8	6.0	12	10	405	3.1	3.1	22
2	2.6	100/0.30	0.36	1.8	5.8	6.0	12	10	1,670	3.1	4.1	18
3	2.6	100/0.15	1.48	3.0	11.8	12.0	42	34	810	0.9	4.2	17
4	12.0	100/0.15	6.80	12.0	35.5	36.0	100	80	530	1.8	2.9	21
5	2.6	400/0.10	0.82	1.3	1.3	3.9	12	10	475	0.77	3.7	23
6	1.48	400/0.10	0.47	1.3	1.3	7.0	24	20	1,490	0.22	3.2	25
7	16.7	1,000/0.20	0.53	1.8	1.8	6.0	51	43	1,130	0.46	4.2	15

In Example 1, a spinneret with holes of .15 mm. diameter was used. Example 2 was carried out in the same manner as Example 1 but with a 100 holes spinneret of .3 mm. size of holes. In both cases, faultless filaments were readily obtained, though for the 0.15 mm. hole size spinneret the rate of delivery was four times the rate of delivery for the .30 mm. spinneret. The stretch between spinneret and washing was 400 and 1600%, respectively.

A comparison of Examples 1, 2, and 3 shows the great elasticity of the process, since with the same apparatus deniers of individual filaments between .9 and 3.1 denier are spun.

Example 4 illustrates the operation with high spinning output.

According to Examples 5 and 6, individual deniers of .77 and .22, respectively, were spun in the same apparatus with a spinneret of 400 holes of size .1 mm. The possibility to spin such fine deniers illustrates the great possibilities of the new process.

Example 7 shows spinning with a 1000 hole spinneret.

None of the examples implies any limitations of my method. A spinneret with .4 mm. holes allows of spinning the same denier under the same conditions as .15 mm. holes, though the difference in the rate of delivery is 700%.

The cold stretchability is greatest as long as the filamentary structures are still impregnated with the acid of the coagulating bath. In the first washing step with dilute nitric acid, the stretchability may be still more than 600%. Then it decreases, and after complete removal of the nitric acid the stretchability increases again only at elevated temperatures.

According to the invention, the coagulation and wet stretching takes place under acid conditions about at room temperature and below, for instance at +30 to −10° C., preferably at 5 to −8° C. Subsequently, heat-stretch may be applied. The total stretch, that is: the wet cold stretching between spinneret and washer under acid conditions, plus the conventional heat-stretching, may attain the huge amount of 10,000 percent of the rate of delivery at the spinneret; this means that it is possible to spin with relatively large-holed spinnerets fast very fine filaments.

The filaments obtained according to the method of the invention are white and silky; they have high tenacity and elongation, and good weather resistance. In a comparative test filaments obtained by my novel method were exposed for 14 months to the atmosphere at Fribourg (640 m. above sea level; 46° northern latitude) on a field 30 cm. above ground. At the end of said period, the loss of strength was only 20 percent of the initial strength. Filaments which had been prepared from the same polymer but had been dissolved in nitric acid with hydrolysis of 20 percent of the nitrile groups and then spun, lost 90 percent of the initial strength under the same conditions.

The invention overcomes the difficulties which heretofore discouraged the use of nitric acid solutions of polyacrylonitrile for spinning operations. The advantages may be summed up as follows:

(1) By the use of nitric acid as solvent, polyacrylonitrile can be converted quickly and very economically into filaments. The solution can be accomplished within a short time at low temperature; ageing or heating of the very viscous spinning solution is not necessary. The solution is fed to the spinneret at the same temperature at which it was obtained. There is no time consuming and complicated heating operation, which is, for instance, required for the preparation of spinning solutions with dimethyl formamide. By means of nitric acid, the polymer powder can be converted within a few hours to filaments of the same chemical composition as the original polymer. In this operation, a temperature of 100° C. is not exceeded, and the pure color of the polymer powder is therefore retained. As the various manipulations do not require much time, the whole plant may be relatively small. There are no corrosion problems because, wherever nitric acid is present, temperatures of 30° C. are not exceeded. A large part of the apparatus can be built from cheap synthetics such as polyvinyl chloride. In view of the low temperatures, no health problems arise with respect to the protection of the operators.

(2) The concentration of the nitric acid withdrawn from the coagulating bath is about 45% HNO_3 and therefore quite close to the concentrations of 54 and 63% required for the solution of the polyacrylonitrile. Therefore, the solvent is readily regenerated by distilling off some water.

(3) The high stretchability in the acid state allows the fast and safe spinning of relatively fine filaments with relatively large holes of the spinneret, that is under relatively low pressure.

(4) The conversion of the polymer into filaments consumes only water and energy, since the nitric acid can be substantially recovered by simple and economic procedures. In addition, nitric acid is cheap in comparison with the organic solvents conventionally used for spinning polyacrylonitrile, and small losses thereof are of little importance.

The discovery that nitric acid in the narrow range of 44–46% HNO_3 is an excellent coagulating bath for nitric acid spinning solutions of polyacrylonitrile, opens the way for the commercial and economic manufacture of polyacrylonitrile filaments from such solutions.

The term "polyacrylonitrile" as used in the specification and claims is intended to designate also polymers which contain at least 80 percent of polyacrylonitrile, the balance being an olefinic compound copolymerizable with acrylonitrile.

I claim:

1. A method of preparing polyacrylonitrile filaments comprising extruding a substantially unhydrolyzed spinning solution of polyacrylonitrile in 56 to 65% HNO_3 through a spinneret into a coagulation bath consisting essentially of aqueous 43–46% HNO_3 and having a temperature of about +30 to −10° C. passing the formed filaments successively through washing zones containing sequentially dilute nitric acid and water, and drawing the freshly formed filaments on their travel from the spinneret to said water washing zone at a rate of at least

400 percent of the rate of extrusion of said solution through said spinneret.

2. The method as defined in claim 1, wherein the filaments are washed first in nitric acid of about 15 to 20 percent HNO_3, then in nitric acid of about 4 to 6 percent HNO_3, and finally in nitric acid of .5 to 2 percent HNO_3.

3. The method as defined in claim 2, wherein the increase of the HNO_3 concentration of said wash solution by the nitric acid of the spinning solution adhering to the filaments is compensated by transfer of weaker nitric acid wash solution from the succeeding washing step.

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