

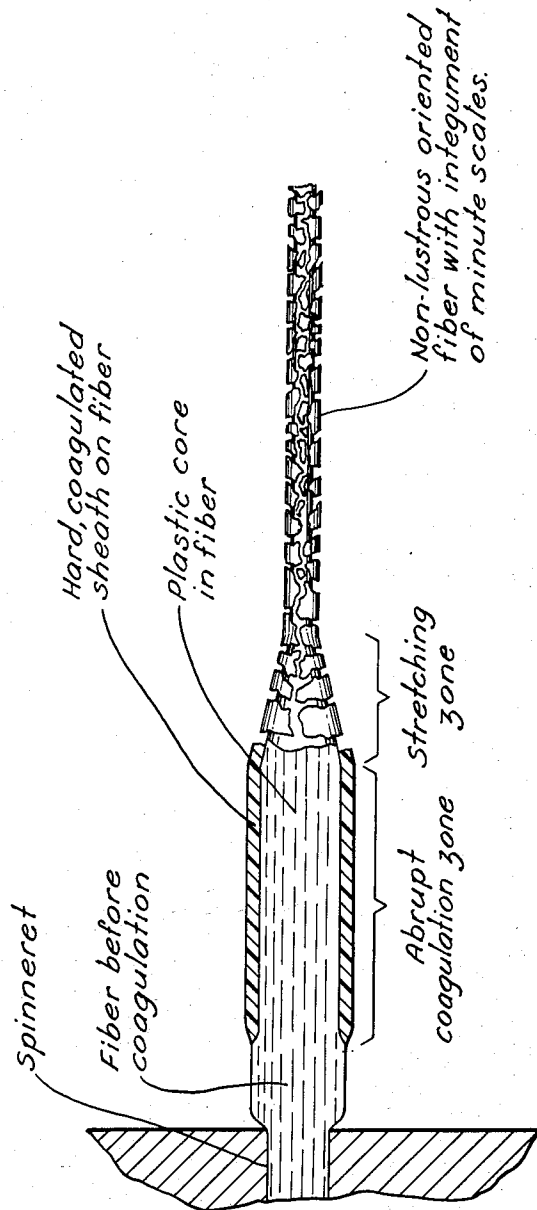
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POLYACRYLONITRILE FIBERS HAVING A SCALY INTEGUMENT

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1

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POLYACRYLONITRILE FIBERS HAVING A SCALY INTEGUMENT

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1 Claim. (Cl. 28—82)

This invention relates to the spinning of polyacrylonitrile fibers from solutions of the polymer in aqueous salts. It relates in particular to a method for producing a fibrous product having the appearance of delustered fibers and having a minute scale-like pattern on the fiber surfaces.

It is well known that polyacrylonitrile, and copolymers generally containing 85 per cent or more of acrylonitrile in the polymer molecule, may be dissolved in aqueous solutions of various salts and that fibers may be made by coagulation of such solutions when they are forced through orifices into non-solvent media. This is disclosed by Rein in U. S. 2,140,921; by Kropa in U. S. 2,356,767 and 2,425,192; by Cresswell in U. S. 2,558,730—735, inclusive; and by the present inventors in co-pending applications, Serial Nos. 228,755—757, inclusive, filed May 28, 1951.

The heretofore disclosed processes for making fibers from aqueous saline solutions of the high acrylonitrile polymers most generally have produced smooth, cylindrical and lustrous fibers. For many purposes it is desirable to have a non-lustrous fiber and one which does not display a smooth and continuous surface. Since it is possible to produce high acrylonitrile polymer fibers having many of the other characteristics of wool fibers, it would be desirable as well to provide the fibers with a surface scale pattern to increase its physical resemblance to wool and to make its behaviour during weaving and in woven goods resemble more closely the behaviour of wool.

It is the principal object of the present invention to provide a method for the spinning of fibers from aqueous saline solutions of polymers containing at least 85 per cent of acrylonitrile in the polymer molecule, such that the spun fibers have a non-lustrous appearance and have a pattern of minute scales over the surface of the fibers.

According to the present invention, the desired results are obtained by extruding an aqueous saline solution of the polymer into an aqueous coagulant at a temperature from 15° to 100° C.; removing the coagulated fibers from the bath after a residence therein of from 0.1 to 3 seconds, sufficient only to form a hard coagulated sheath on the fibers; and, at any stage in the process while the core of the fibers is still plastic, stretching the fibers to rupture the initially coagulated sheath, and extracting residual salt from the fibers.

The coagulation is very abrupt, and a hard shell is formed instantly on each fiber before the salt can be leached from the core, which remains relatively plastic. The coagulant may be water alone, or wet steam at 100° C., or it may be water containing a salt such as sodium chloride which is a non-solvent for the polymer, or a dilute solution, below solvent concentrations, of a salt which, at much higher concentrations, is a solvent for the polymer, or a dilute acid, or an organic but water-miscible coagulant such as acetone, methanol or ethanol dissolved in water. In any case, the coagulant is water or may be said to comprise mainly water. The duration

2

of the initial abrupt coagulation need not exceed 3 seconds, and, at the higher temperatures in the operative range, may be as brief as 0.1 second. When using a severe coagulant, such as water or steam at a temperature near 100° C., a very short residence is required in the coagulating zone, of the order of 0.1 second. In such case, most of the stretching will be effected in a subsequent zone, while the outer sheath is still hard and the core is still plastic. When using less severe coagulating conditions, such as exposure to water at 15° C., a residence time of the order of 3 seconds may be required to form the hard sheath, and much of the stretching can be done while the fiber is in the coagulating bath.

Following or during the abrupt coagulation, the fibers may be stretched to rupture the sheath into minute scale-like patterns, but it is preferred to pass them through an aqueous bath at a lower temperature than that at which initial coagulation occurred, suitably at 10° to 35° C., to reduce the salt concentration in the core of the fiber and to redistribute the remaining salt throughout the fiber. While the core is still plastic as compared with the relatively hard outer sheath, the fibers are stretched in any conventional way, in aqueous baths, in air or in wet steam, to effect the desired elongation and orientation. Thereafter, the usual finishing steps are carried out, including any necessary final salt removal, drying and the various yarn making operations. The product is found, by microscopic examination, to have a surface pattern of small scale-like protuberances which effectively disperse incident and transmitted light, making the fiber non-lustrous, and giving it a superficial roughness resembling that of wool fibers.

The following examples illustrate the practice of the invention:

Example 1

A 10 per cent solution of polyacrylonitrile in a solvent medium consisting of 35 per cent by weight of zinc chloride, 26 per cent calcium chloride and 39 per cent water, was used for fiber formation. The solution was spun through a spinneret having 60 holes, each 0.003 inch in diameter, into water at 25° C. The resulting fibers were withdrawn from the bath after a residence therein of about 1 second and were then stretched 2.5 times their original length and were led through a water bath at 25° C. After 15 seconds in this bath, the fibers were stretched 170 per cent to 4.25 times their original length per unit weight, in saturated steam at 100° C., becoming non-lustrous during the stretching. They were then soaked in cold water to remove as much salt as possible, and were dried under tension. The resulting fibers were non-lustrous and had an integument of fine scales which could be seen under a microscope and which gave them a feeling of being slightly rough to the touch, in the way that wool feels rough.

Example 2

Some of the solution employed in the preceding example was spun into water at 25° C. and, after 2 seconds, the fibers had a hard shell and were conducted through a second bath consisting of 55 per cent water, 26 per cent zinc chloride and 19 per cent calcium chloride. The residence time in the latter bath, at 25° C., was 10 seconds. The so-conditioned fibers were removed from the bath and stretched in air to 4 times their original length. They were then washed with water until essentially free from salts, and were dried. The resulting fibers were non-lustrous and had a fine scaly coating which could be seen under a microscope.

Example 3

An 11 per cent solution of polyacrylonitrile in a 60

3

per cent solution of zinc chloride in water was spun through a 60-hole spinneret, each orifice of which was 0.006 inch in diameter. The coagulating bath was a 15 per cent solution of zinc chloride in water at 25° C. The so-hardened fibers remained in the coagulant 2 seconds, and were stretched 200 per cent just before emerging from the bath. They were then washed in cold water at 10° C. until essentially free from zinc chloride and were immersed in water at 100° C. and stretched an additional 350 per cent. When dried, the so-treated fibers were non-lustrous and had the previously described scaly integument.

Example 4

Some of the polymer solution employed in Example 3 was spun through the same spinneret into a mist of condensing steam at 80° to 95° C. While in this atmosphere the fibers acquired a hard sheath, and they were stretched 200 per cent in the coagulant. The fibers were washed free from zinc chloride in cold water and were immersed in boiling water and stretched an additional 350 per cent therein. When dried, the fibers had the non-lustrous appearance, and the coating of microscopic scales previously described.

The invention is illustrated in the annexed drawing which shows the extrusion of the spinning dope into an abrupt coagulation zone in which a hard sheath is formed on the cylindrical fiber which still retains a fluid or plastic core, the stretching of the fiber with rupture of the sheath, and the non-lustrous stretched fiber having

4

a covering of minute scales. The microscopic scales are greatly exaggerated for the purpose of the illustration.

The new fibers may be described as monophyletic, because they have a single source or are developed from a single common parent form, and they are monoplasmatic, being composed of the same substance in their axial core and in the protuberances or scales forming the integument about said core.

We claim:

A monophyletic and monoplasmatic non-lustrous cylindrical fiber having an axial core and a scaly integument, the fiber being composed of a polymer containing at least 85 per cent by weight of acrylonitrile in the polymer molecule, the said integument consisting of microscopically fine irregular scale-like protuberances from the axial core, serving to roughen the fiber and to disperse incident and transmitted light.

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