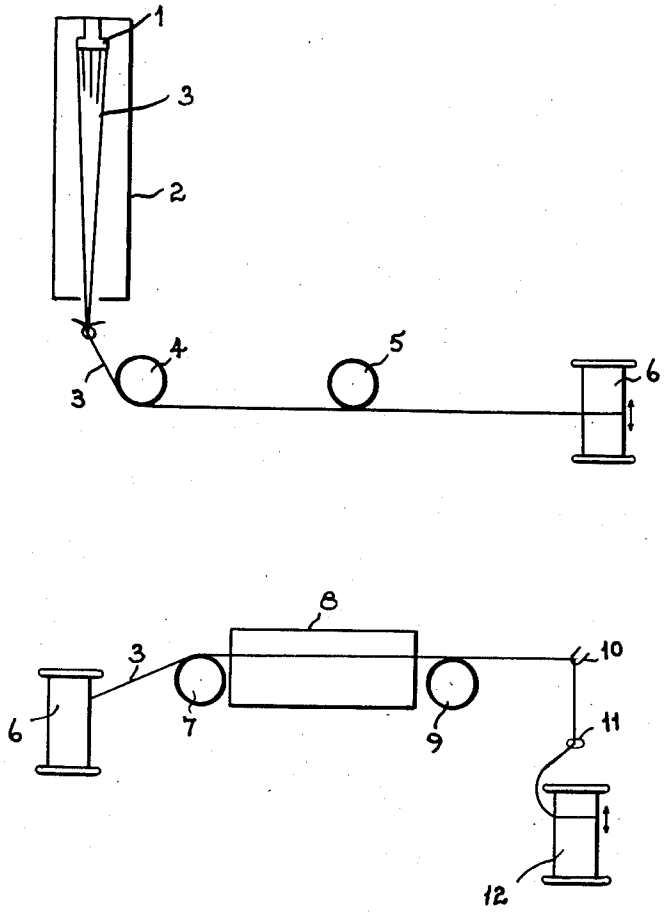
Nov. 27, 1962 A. S. CARPENTER ETAL 3,066,008

PROCESS FOR PRODUCING FIBERS FROM COPOLYMERS OF ACRYLONITRILE AND VINYLIDENE CHLORIDE

Filed Feb. 25, 1960



INVENTORS
ALBERT S. CARPENTER
RICHARD N. TIMMS

BY Howson and Howson

ATTORNEYS

United States Patent Office 3,066,008 Patented Nov. 27, 1962

3,066,008

PROCESS FOR PRODUCING FIBERS FROM COPOLYMERS OF ACRYLONITRILE AND VINYLIDENE CHLORIDE

Albert Stanley Carpenter, Sutton Coldfield, Birmingham, and Richard Neville Timms, Coventry, England, assignors to Courtaulds Limited, London, England, a British company

Filed Feb. 25, 1960, Ser. No. 10,880
Claims priority, application Great Britain Mar. 9, 1959
8 Claims. (Cl. 18—54)

This invention relates to the manufacture of synthetic fibres and is particularly concerned with the manufacture of fibres from the copolymers of acrylonitrile and vinylidene chloride which are soluble in acetone. The invention is applicable to acetone-soluble binary copolymers of acrylonitrile and vinylidene chloride and also acetone-soluble copolymers of the two compounds with small amounts, for example up to about 5 percent by weight, of other monomers such as vinyl pyridine or itaconic acid which may be used to modify the dyeing properties of the copolymer.

Proposals have already been made to produce acetone-soluble copolymers of acrylonitrile and vinylidene chloride, see for example British patent specification No. 643,198 and the Carpenter application Serial No. 788,045, now Patent No. 3,004,008. The acetone solutions of the copolymers may be wet or dry spun to form fibres as described for example in British patent specification No. 674,323 of British Celanese Limited. This latter specification also describes the step of stretching the resultant fibres in a heat-softened condition, for example in a hot water bath or in saturated steam; the stretching step may be followed by an annealing treatment so as to reduce the tendency of the fibres to shrink when heated to moderately elevated temperatures such as 60° to 100° C. A further type of stretching of the acrylonitrile-vinylidene chloride copolymer fibres is described in the Hampson et al. Patent No. 2,679,450 according to which the fibers are stretched at a temperature above 120° C., for example in steam or hot water under pressure.

We have now found that it is particularly advantageous if the freshly extruded fibres of acrylonitrile-vinylidene chloride copolymers are subjected to a cold stretching operation before they are collected. The term "cold stretching" means that the fibres are stretched at a temperature not greater than 40° C. In general, for economic reasons, the fibres are stretched at the ordinary temperatures. The degree of stretching should be at least 75 percent and may conveniently be from 100 to 300 percent. Throughout this specification the degree of stretching is expressed as the percentage of the increased length on the original length of the fibre; for example for a fibre stretched to twice its original length the stretch is 100 percent.

The cold stretching of the freshly extruded fibres is preferably effected between godets, the fibres leaving the spinning cell or the coagulating bath, as the case may be, being passed round a first godet and then to a second godet the peripheral speed of which is arranged to give the fibres the required degree of stretching. However, other known methods of stretching, for example using reels or rollers, or a combination of a godet and reel, may be used. Once the fibres have been cold stretched shortly after their extrusion they are preferably collected on bobbins either as twisted or untwisted yarns ready for further processing, but they may be further processed in a continuous operation.

The cold stretching is preferably effected in air, particularly when dry spun fibres are being stretched, but stretching may be effected in water or other non-solvent

at 15–40° C., and the liquid may contain a textile lubricant.

One effect of the cold stretching operation is to make the fibres less rubbery in character. A second effect is to reduce appreciably or to eliminate entirely the risk of stuck filaments in the collected yarn.

The fibres produced by the cold stretching operation are not however suitable for general textile uses and they are therefore given a further stretch treatment at elevated temperature. Such further stretching should be from 500 to 2,000 percent and preferably 700 to 1,500 percent. Suitable elevated temperatures are temperatures not less than 95° C. Such hot stretching may be carried out in hot air, steam or hot water under pressure as described in the above mentioned British specification No. 674,323 and United States Patent No. 2,679,450, and the hot stretching process may be followed by an annealing treatment to reduce the shrinkage of the fibre on heating. According to a preferred embodiment of this invention the hot stretching treatment is carried out at temperatures above 100° C. using saturated steam at superatmospheric pressure, for example up to 50 lbs. per square inch, as the heating medium. The fibres obtained as a result of stretching the cold-stretched fibres in saturated steam at superatmospheric pressure have high dimensional stabilities to wet and dry heat which are adequate for many textile purposes. In general, the fibres so stretched contract only a few percent in boiling water or in air at 136° C. and, moreover, a marked improvement in colour stability on exposure to dry heat is also obtained. If desired, still further stabilization can be effected by an annealing treatment carried out by immersing the fibres in hot or boiling water, in open steam, in steam under pressure or in hot air while allowing the natural contraction of the fibre to take place freely. For example, the fibres, after the stretching treatment in saturated steam at superatmospheric pressure, may be passed continuously, under conditions of free relaxation, through a bath of water at, or near, its boiling point (that is to say at about 90–100° C.), or through a tube containing saturated steam at atmospheric pressure. The resulting fibres show virtually no contraction on subsequent immersion in boiling water.

The present invention is illustrated by the accompanying drawings. The acetone solution of the acrylonitrile-vinylidene chloride copolymer is extruded through a jet 1 within a spinning cell 2 to form filaments 3; hot air is continuously circulated within the cell 2 in known manner. The filaments 3 leaving the cell 2 are lapped round a godet 4 and are passed directly to a second godet 5 moving at a peripheral speed designed to stretch the filaments at least 75 percent in air between the two godets. From the godet 5 the filaments 3 are collected, without twist, on a bobbin 6.

In order to obtain the desired increase in tensile strength, the cold stretched filaments are hot stretched. Thus the filaments 3 are withdrawn from the bobbin 6 and lapped round a godet 7 before being drawn through a steam chest 8 by a godet 9 which stretches the filaments in contact with the steam at least 500 percent. The hot stretched filaments are then passed by way of guides 10, 11 to a ring spinning machine where a bobbin 12 of twisted filaments is collected.

The invention is illustrated by the following examples.

Example 1

A copolymer of acrylonitrile and vinylidene chloride produced according to the method described in the Carpenter application Serial No. 788,045, now Patent No. 3,004,008, and having an acrylonitrile content of 51 percent and an intrinsic viscosity of 1.47 in dimethyl form-

amide solution was dissolved in acetone to give a 22 percent by weight solution. This solution was dry spun on conventional dry spinning equipment and the resulting fibres leaving the spinning cell were cold stretched 100 percent between godets and were then collected, untwisted, on a bobbin. The final collection speed was 40 metres per minute and the denier was 266. Examination of the collected yarn showed no stuck filaments and the yarn could be removed from the bobbin without difficulty, even after prolonged storage.

The yarn was then withdrawn from the bobbin and passed continuously, with stretching, through saturated steam at 30 lbs. per square inch using an apparatus consisting of two adjoining chambers, containing respectively hot water under pressure and then steam under pressure, and was finally collected as a twisted yarn. The yarn was passed into the water through a plate containing a fine orifice, and from the water into the steam through a second orifice and out of the steam through a third orifice. A godet fed the yarn to the apparatus at 2.0 metres per minute and a second godet removed it at 20.0 metres per minute and thus imposed a 900 percent stretch. The stretching tension was 2 grams. The denier of the collected yarn was 26, its tenacity was 4.35 grams denier, its extensibility was 10.7 percent and its contraction on immersion in boiling water for 15 seconds was 4.6 percent. The cold-stretched yarn before the hot stretching process had a tenacity of 1.47 grams/denier, an extensibility of 53.8 percent and a contraction in boiling water of 37 percent.

The yarn was finally passed continuously through a bath of boiling water under conditions of free relaxation, the immersion time being 11 seconds. Its tenacity was then 3.40 grams/denier, its extensibility 13.8 percent and its contraction in boiling water about 0.5 percent; it showed no contraction on being heated in air at 136° C. for 1 hour.

Example 2

A copolymer of acrylonitrile and vinylidene chloride was produced by the method described in the Carpenter application Serial No. 788,045, now Patent No. 3,004,008, the copolymer containing 47 percent by weight of acrylonitrile and having an intrinsic viscosity, measured in dimethyl formamide, of 1.73. It was dissolved in acetone to produce a 22 percent by weight solution which was then dry spun through a 40 hole jet as described in Example 1 to produce fibres which were stretched 100 percent at ordinary temperatures between a godet and a thread-advancing reel and then collected on bobbins without twist. The collected yarn was 900 denier/40 filament yarn.

The yarn was withdrawn from the bobbin by a godet having a peripheral speed of 4 metres/minute and stretched 1,150 percent in saturated steam at 20 lbs. per square inch by a second godet of peripheral speed 50 metres/minute; it then passed continuously at 50 metres/minute through an atmosphere of saturated steam at atmospheric pressure to a godet of peripheral speed 47 metres/minute and finally collected as a twisted yarn on a ring twisting machine.

The yarn obtained had a tenacity of 4 grams/denier and an extensibility of 14 percent. It was dimensionally stable to dry and wet heat. It was woven into a fabric which was found to be flame-proof according to the British standards specification. Samples of the fabric were unaffected by contact for 5 seconds with a hot iron at temperatures up to 220° C.

What we claim is:

1. In a process for the production of fibres by extruding an acetone solution of a copolymer of acrylonitrile and vinylidene chloride through a jet into an evaporative atmosphere within a spinning cell to form fibres and withdrawing the fibres so formed from the spinning cell, the step of cold stretching the fibres in air continuously with their withdrawal from the cell from 75 to 300 percent at a temperature in the range of 15° to 40° C.

2. A process as claimed in claim 1 wherein the fibres are stretched from 100 to 300 percent.

3. In a process for the production of fibres by extruding an acetone solution of a copolymer of acrylonitrile and vinylidene chloride through a jet into an evaporative atmosphere within a spinning cell to form fibres and withdrawing the fibres so formed from the spinning cell, the steps of cold stretching the fibres in air continuously with their withdrawal from the cell from 75 to 300 percent at a temperature in the range of 15° to 40° C., collecting the stretched fibres on a bobbin and subsequently withdrawing the fibres from the bobbin and stretching them a second time from 500 to 2000 percent at a temperature not less than 95° C.

4. A process as claimed in claim 3 wherein the fibers are stretched in saturated steam at superatmospheric pressure.

5. A process as claimed in claim 3 wherein the freshly-extruded fibers are first stretched from 100 to 300 percent at a temperature in the range of 15° to 40° C. and then from 700 to 1,500 percent at a temperature not less than 95° C.

6. A process as claimed in claim 3 wherein the hot-stretched fibres are subjected to an annealing treatment in which they are heated while allowing the natural contraction of the fibres to take place freely.

7. A process as claimed in claim 6 wherein the annealing treatment is effected in a bath of water at 90° C. to 100° C.

8. A process as claimed in claim 6 wherein the annealing treatment is effected in saturated steam at atmospheric pressure.

References Cited in the file of this patent

UNITED STATES PATENTS

2,420,565	Rugeley	May 13, 1947
2,681,265	Hoxie	June 15, 1954
2,697,023	Martin	Dec. 14, 1954
2,716,586	Terpay	Aug. 30, 1955
2,775,507	Downing	Dec. 25, 1956