METHOD FOR MANUFACTURING IMPROVED ACRYLONITRILE FILAMENTS

Filed Feb. 7, 1968

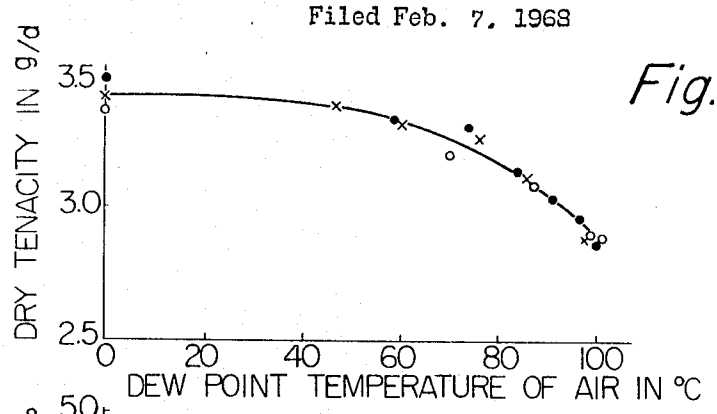


Fig. 1

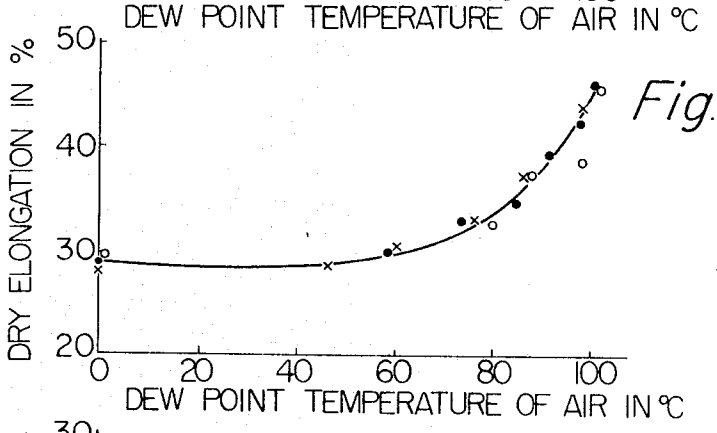


Fig. 2

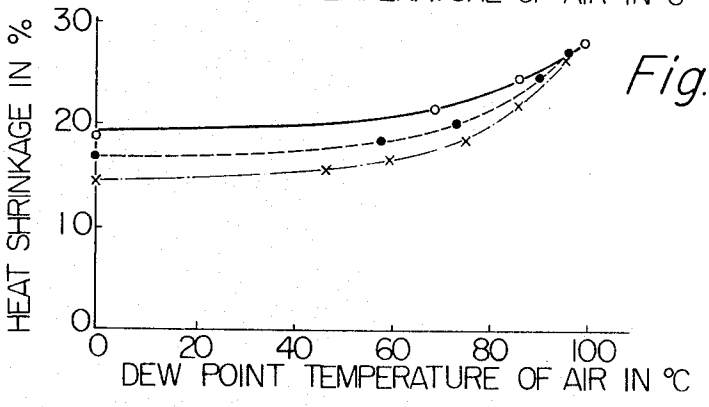


Fig. 3

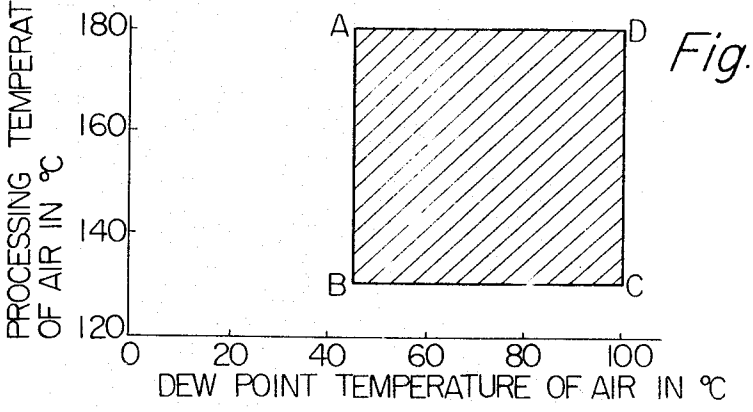


Fig. 4

United States Patent Office 3,514,512 Patented May 26, 1970

3,514,512

METHOD FOR MANUFACTURING IMPROVED ACRYLONITRILE FILAMENTS

Shigeru Kikuchi, Keishiro Ueno, Shoji Imao, and Makoto Tanaka, Otake-shi, Japan, assignors to Mitsubishi Rayon Co., Ltd., and Mitsubishi Vonnel Co., Ltd., both of Tokyo, Japan, both companies of Japan

Filed Feb. 7, 1968, Ser. No. 703,690
Claims priority, application Japan, Feb. 9, 1967, 42/8,452
Int. Cl. B29c 25/00
U.S. Cl. 264—342 10 Claims

ABSTRACT OF THE DISCLOSURE

A method for manufacturing acrylonitrile filaments having improved properties and substantially void-free structure by applying a relaxation treatment upon stretched filaments using humid medium of a definite temperature and humidity while the filaments are still in the swollen condition. The manufactured filaments are provided with superior physical properties, good hand feeling, excellent whiteness and improved apparent transparency caused by the collapse of the voids formed in the filament structure.

The present invention relates to a method for manufacturing acrylonitrile filaments having improved physical properties and substantially void-free structure, more particularly relates to a method for manufacturing acrylonitrile filaments having improved physical properties and substantially void-free by spinning the solution of acrylonitrile polymer into filaments by means of the dry- or wet-spinning process and, thereafter, applying relaxation treatment on the filaments in humid medium of a definite temperature and humidity simultaneously with drying while the filaments are still in the swollen condition.

The term "wet-spinning" as used herein includes so-called dry-wet spinning.

As is well-known, in case acrylonitrile filaments are manufactured by the wet spinning process associated with stretching treatment in boiling water, the filaments obtained are generally provided with numerous voids. This is also the case with acrylonitrile filaments manufactured by the dry spinning process associated with elimination of solvents or with stretching in hot water. The formation of such voids is liable to result in unfavorable apparent turbidity, easy fibrillation and very poor dyeability of the filament obtained. Such ill effects caused by the inevitable formation of voids is generally believed to be reduced by collapsing the voids formed within the filaments.

Generally, this collapsing void is practically performed by passing the filaments over a heated solid surface after spinning under a stressed condition but this requires a higher temperature in the following relaxation treatment and as a result, deterioration in whiteness and hand feeling of the filaments is produced. It is also possible to carry out the collapsing voids by applying relaxation treatment with steam on the filaments after spinning. However in this case, it is difficult to make the entire production process continuous because of the fact that utilization of high pressure steam is required for the relaxation treatment.

Many methods have been proposed in order to overcome the difficulties encountered in the traditional technique for collapsing the voids formed within the filaments.

The process disclosed in the Japanese patent publication No. 8,473/57 is one of the examples, wherein the

acrylic filaments in gell condition are dried at a temperature from 93° C. to 127° C. in order to improve the dyeability, anti-frictional property hand feeling and anti-fibrillation of the filaments manufactured. A process of the same scope is disclosed in the Japanese patent publication No. 1,828/65, wherein the filaments are stretched again at a stretching ratio from 1.1 to 1.5 after being dried in the same manner as that disclosed in the Japanese patent publication No. 8,473/57. Another method for collapsing the voids is found in the process disclosed in the Japanese patent publication No. 13,698/65 which comprises drying acrylic hollow filaments in a swollen gell condition in a humid atmosphere maintained at a temperature from 30 to 70° C. and relative humidity from 40 to 100%. However, these methods are also accompanied by several drawbacks. The first of these is that too long processing time is required for the treatment of the filament because of lower treating temperature of the method. And the second of these is that the filament obtained is not provided with satisfactory dimensional stability.

The principal object of the present invention is to provide a novel method for manufacturing acrylonitrile filaments having improved physical properties and substantially void-free structure by eliminating the drawbacks encountered in the conventional methods for manufacturing the same.

The other object of the present invention is to provide a novel method for manufacturing acrylonitrile filaments having superior apparent transparency, good hand feeling, excellent whiteness and improved dyeability.

Further object of the present invention is to provide a novel method for manufacturing acrylonitrile filaments having improved properties which can be effectively in practical continuous process with lower thermal consumption and pressure resulting in lower production cost due to higher processing efficiency.

In order to attain the objects of the invention, the method of the present invention comprises, spinning the solution of acrylonitrile polymer into filaments, stretching thus formed filaments and thereafter, applying relaxation treatment upon the stretched filaments while simultaneously drying the stretched filaments, whose moisture regain is maintained at above 15%, under relaxed condition with humid air maintained at a dew point temperature from 45 to 100° C. and a processing temperature from 130 to 180° C. The degree of the moisture regain of the filaments supplied to the relaxation treatment differs in accordance with the type of the spinning process, that is, it is preferably higher than 50% for the wet spinning process while it is between 15 and 100% in case of the dry spinning process. In case of the so-called dry-wet spinning process, it is recommended that moisture regain of the former be used.

As a medium used for drying the filaments, not only air but also gases such as inert gas or exhaust gas mainly composed of carbon dioxide or nitrogen can suitably be used. Sometimes such gases are more preferable than air in order to prevent discoloration of the filaments by heating or excessive consumption of thermal energy.

As the acrylonitrile polmer used for the purpose of the present invention, not only acrylonitrile homo-polymer but also acrylonitrile co-polymers containing more than 80% by weight of acrylonitrile or their blended polymers can preferable be used. While these acrylonitrile polymers are manufactured by any of the well-known spinning processes including the so-called composite spinning process, the wet- or dry-spinning process is recommended, depending on the object of the present invention.

Although any of the well-known solvents is available for dissolving the acrylonitrile polymers in the present inven-

tion, solvents such as dimethyl formamide dimethyl acetamide, dimethyl sulfoxide or γ-butyrolactone can most preferably be used as the solvent for acrylonitrile polymers.

After spinning, the filaments undergo washing, stretching and relaxation treatment while drying. Washing of the filaments should preferably be performed in hot water of 30 to 90° C., generally, followed by stretching at a stretching ratio from 2 to 7 times in hot water of 70 to 100° C. Stretching of the filaments can be also carried out simultaneously with washing. It is also possible to carry out washing of the filaments in hot water of 60 to 100° C. after the stretching treatment. In carrying out washing, it should be noted that the content of the solvent within the filaments should be maintained lower than 3% by weight, or more preferably lower than 1.5% by weight, of the filaments after washing and stretching. In case the content of the solvent is too high, it causes excessive loss of solvent, discoloration of the filaments during the following relaxation and drying process, remarkably increased shrinkage by heat of the filaments and unfavorable effects on the physical properties of the filaments manufactured.

In case the filaments are manufactured by the wet spinning process, the moisture regain of the filaments before the application of the drying process should be higher than 50% in order to obtain filaments of superior quality.

While the heat shrinking percentage of the filaments is constant for a moisture regain higher than 50%, it decreases gradually with reduction in moisture reagain when the moisture regain becomes lower than 50% and the stress-strain property of the filaments manufactured varies in accordance with this reduction in the heat shrinking percentage.

In case of the dry spinning process, a moisture regain above 15% is sufficiently high to obtain filaments of superior quality. This is mainly because of the fact that a stable net-like configuration of polymers is formed within the filament due to the rather moderate formation of the filaments in the dry spinning compared with that in the wet spinning process, and that the stable net-like configuration of polymers thus formed provides the filaments with less shrinkage in relaxation treatment, and therefore there is there is little deterioration in the anti-fibril property or dyeability even with lower elongation of the filament.

After the stretching treatment, relaxation treatment is then applied simultaneously with drying with the humid medium maintained at a dew point temperature from 45 to 100° C. and a processing temperature from 130 to 180° C. to the stretched filaments having moisture regain higher than 50% in case of the wet spinning process while the stretched filaments having a moisture regain higher than 15% is supplied to the relaxation process under the same processing condition in case of the dry spinning process.

Further features and advantages of the present invention will be apparent from the ensuing description with reference to the accompanying drawings to which, however, the scope of the invention is in no way limited.

FIG. 1 is a graphical drawing for showing the relation between the tenacity of a manufactured filament and the dew point temperature of humid air used for the relaxation treatment of the filament,

FIG. 2 is a graphical drawing for showing the relation between the elongation of a manufactured filament and the dew point temperature of humid air used for the relaxation treatment of the filament,

FIG. 3 is a graphical drawing for showing the relation between the heat shrinking percentage of a manufactured filament and the dew point temperature of humid air used for the relaxation treatment of the filament,

FIG. 4 is a graphical drawing for showing the relation between the processing temperature and the dew point temperature of humid air used for the relaxation treatment of the filaments.

Referring to FIGS. 1 and 2, the tenacity and elongation of the manufactured filaments is shown at various dew point temperature and processing temperature of the

humid air used for the relaxation treatment of filaments. In the drawings, the tenacity and elongation of the manufactured filaments measured at various processing temperatures of the humid air is taken on the ordinate and the corresponding dew point temperature of the humid air is taken on the abscissa, and the plot marked with the symbol (○) is for the processing temperature of 160° C., the symbol (●) is for 140° C. and the symbol (X) is for 120° C. As it is apparent from the experimental results shown in the graphical drawings, the tenacity and elongation of the manufactured filament is affected only by the dew point temperature of the humid air used for the relaxation treatment of the filament. In other words, the processing temperature of the humid air does not play an important role in determining the tenacity and elongation of the manufactured filaments provided that the other processing conditions of the filaments before drying remain the same.

Next, the heat shrinkage property of the manufactured filaments in relation to the dew point temperature and the processing temperature of the humid air is shown in FIG. 3, wherein the full line is for the processing temperature of 160° C., the dotted line is for 140° C. and the dash-and-dot line is for 120° C. The relation illustrated in the drawing is characterized by the fact that the heat shrinkage property of the manufactured filaments is slightly affected also by the processing temperature of the humid air used for the relaxation treatment while it is mainly affected by the dew point temperature of the humid air. The heat shrinkage during the relaxation and drying treatment of the present invention is generally between 15 and 30%.

The preferable processing temperature of the humid air used for the relaxation and drying treatment of the present invention lies between 130 and 180° C. By selecting the processing temperature in this range, it is possible to carry out the process within 1 to 15 minutes which is of a great advantage in the actual production process, and this length of processing time is long enough to collapse the voids formed within the filaments. In case the processing temperature of the wet air becomes higher than 180° C., discoloration of the filaments can be expected to take place during the treatment, resulting in poor appearance of the manufactured filaments. Consequently, the optimum processing condition during the relaxation and drying treatment of the present invention is within the shaded portion in the drawing of FIG. 4, wherein the processing temperature is taken on the ordinate and the dew point temperature of the wet air used for the treatment on the abscissa. In the drawing, the corner A is for a processing temperature of 180° C. and a dew point temperature of 45° C., the corner B is for 130° C. and 45° C., the corner C is for 130° C. and 100° C. and the corner D is for 180° C. and 100° C., respectively.

In order to obtain a better result in the relaxation and drying treatment of the present invention, it is recommended that crimps be imparted to the filaments by a suitable mechanical method prior to the relaxation and drying treatment. By imparting such crimps, the circulation of the humid medium through the filament is remarkably improved to permit rapid and uniform relaxation. And the crimps imparted to the filaments are heat-set in the relaxation and drying treatment and thus the hand-feeling of end products from the filaments are improved. The latter effect is not obtained in case the processing temperature of the humid air is lower than 130° C. Crimps of this kind can be imparted by any of the known methods, for instance, using a stuffing-box type crimper.

The dry and relaxation treatment of the present invention can be performed under atmospheric pressure requiring no special installation of pressure equipments. Therefore the treatment of the present invention can easily be inserted or added to the conventional production system of synthetic filaments at low installation expense. This is one of the outstanding advantages of the present invention. Besides, the method of the present invention

greatly contributes to the simplification of the practical production system of system of synthetic filaments resulting in high production efficiency because drying of the filaments can be performed simultaneously with the relaxation treatment. This is another outstanding advantage of the present invention.

In order to prevent the separation of the bundle of filaments during the process of the present invention, it is desirable to apply pre-relaxation upon the filaments before drying, for instance by treating them with boiling water or heated steam. It is also recommended that heated steam be supplied into a stuffing-box in order to subject the filaments to pre-shrinkage treatment simultaneously with crimping. The degree of the pre-shrinkage subjected to the filaments should be determined such that the total shrinkage of the filament after the dry and relaxation treatment is preferably between 18 and 35%. When the amount of the pre-shrinkage is large enough, there will be little shrinkage of the filaments in the dry and relaxation treatment resulting in less separation of the bundle of filaments. In this case, the dry and relaxation treatment can effectively contribute only to collapsing the voids within the filaments which is the principal object of the present invention.

The dry and relaxation treatment of the present invention can be carried out by using any of the well-known conventional type of drying equipment such as the drum type or the net conveyer type and the dew point temperature of the humid air can be effectively maintained at a constant value by using a suitable photo-electric device.

The following examples are illustrative of the present invention but are not to be construed as limiting the same.

EXAMPLE 1

A spinning solution containing 20.5% by weight of polymer component was prepared by dissolving a co-polymer composed of 95% of acrylonitrile and 5% of vinyl acetate with dimethyl formamide. This spinning solution was extruded through the spinnerets at a spinning speed of 4 m./min. into an aqueous coagulating bath containing 40% by weight of dimethyl formamide and maintained at a temperature of 30° C. to form filaments. After washing the filaments were stretched in boiling water of 100° C. at a stretching ratio of 5.0 and then oil was applied. The moisture regain of the oiled filaments in a swollen gell condition was adjusted to 120%. Then dry and relaxation treatment was applied to the filaments with heated humid air maintained at various dew points and processing temperatures for 10 minutes as shown in the following table. Several resulting properties of the thus treated filaments are shown in the table with the corresponding temperatures of the air, and results are shown graphically in the drawings of FIGS. 1, 2 and 3.

TABLE

Manufacturing method	Processing temperature of the humid air, in ° C,	Dew point temperature of the humid air, in ° C,	Heat shrinkage, in percent	Dry tenacity, in g./d.	Dry elongation, in percent	Shrinkage in boiling water, in percent [1]
Control	120	0	14.2	3.43	28.1	6.4
Do	120	46.2	15.8	3.41	28.6	2.4
Do	120	60.0	16.8	3.33	30.9	1.4
Do	120	75.7	18.6	3.27	33.5	0.7
Do	120	85.7	22.3	3.12	37.6	0.4
Do	120	97.2	27.0	2.91	44.4	0.1
Do	140	0	16.8	3.51	29.1	3.5
Invention	140	58.5	18.5	3.35	30.1	1.7
Do	140	73.7	20.0	3.32	33.3	1.0
Do	140	83.8	22.6	3.16	35.0	0.4
Do	140	90.8	24.3	3.05	39.5	0
Do	140	96.8	27.3	2.98	42.7	[2] −0.3
Do	140	100	27.8	2.88	46.5	−1.0
Control	160	0	19.1	3.39	29.5	0.2
Invention	160	69.5	21.5	3.21	33.0	−0.1
Do	160	86.6	24.1	3.10	37.6	−0.4
Do	160	97.5	27.0	2.91	39.0	−0.6
Do	160	100	27.8	2.85	46.0	−0.8

[1] This value is considered as an index for showing the dimensional stability of the manufactured filaments.
[2] In case this value is in the minus region, the filament is regarded as being elongated in boiling water,

The collapsing of the voids formed within the filaments was realized sufficiently in case the processing temperature of the air was over 130° C. and the dew-point temperature of the air was over 45° C.

EXAMPLE 2

A spinning solution containing 31% by weight of polymer component was prepared by dissolving a co-polymer having an intrinsic viscosity of 1.50 and composed of 94.0% of acrylonitrile, 5.2% of methyl acrylate and 0.8% of sodium methallylsulfonate with dimethyl formamide. This spinning solution was extruded through the spinnerets provided with 50 spinning holes of 0.1 m./m. dia. into heated air of 220° C. to form filaments and taken up at a speed of 240 m./min. The taken-up filaments contained about 9% by weight of the solvent. While washing the filaments in boiling water, the filaments were stretched at a stretching ratio of 6.5. Then dry and relaxation treatment was applied to the filaments for 10 minutes with humid air maintained at a dew point temperature of 97° C. and a processing temperature of 140° C. The moisture regain of the filaments before treatment was 75% and the heat shrinkage of the filament during the treatment was 26.8%. The manufactured filament was provided with a tenacity of 3.20 g./d., elongation of 34.0% and also with excellent dyeing affinity for basic colours.

While the present invention has been described in conjunction with certain embodiments thereof, it is to be understood that various modifications and changes may be made without departing from the spirit and scope of the invention.

What is claimed is:

1. A method for manufacturing substantially void free acrylonitrile filaments comprising: providing acrylonitrile filaments containing numerous voids therein and having a moisture regain greater than 15%; and subjecting the acrylonitrile filaments simultaneously to a drying and relaxation treatment in a humid medium having a dew point temperature within the range of 45 to 100° C. and processing temperature within the range of 130 to 180° C. to effectively collapse the voids.

2. A method according to claim 1; further including, prior to the providing step, wet spinning an acrylonitrile polymer solution into acrylonitrile filaments containing numerous voids therein; and wherein said providing step has a moisture regain greater than 50%.

3. A method according to claim 1; further including maintaining the heat shrinkage of said acrylonitrile filaments during said drying and relaxation treatment between 15 to 30%.

4. A method according to claim 1; further including, prior to said drying and relaxation treatment, subjecting the provided acrylonitrile filaments to a pre-shrinkage treatment.

5. A method according to claim 4; further including maintaining the total heat shrinkage of said acrylonitrile filaments during said drying and relaxation treatment between 18 to 35%.

6. A method according to claim 1; further including crimping said acrylonitrile filaments prior to said drying and relaxation treatment.

7. A method according to claim 1; further inclluding, prior to the providing step, dissolving an acrylonitrile polymer with an organic solvent; spinning the acrylonitrile polymer solution into acrylonitrile filaments containing numerous voids therein; and reducing the solvent content contained within said acrylonitrile filaments to less than 3.0% by weight.

8. A method according to claim 8; further including reducing said solvent content to less than 1.5% by weight.

9. A method according to claim 1; further including, prior to the providing step, dissolving an acrylonitrile polymer with an organic solvent; and wet spinning the acrylonitrile polymer solution into acrylonitrile filaments containing numerous voids therein.

10. A method according to claim; further including, prior to the providing step, dissolving an acrylonitrile polymer with an organic solvent; and dry spinning the acrylonitrile polymer solution into acrylonitrile filaments containing numerous voids therein.

References Cited

UNITED STATES PATENTS

3,101,245	8/1963	Fujita et al.	264—182 X
3,404,204	10/1968	Nakagawa et al.	264—182
3,433,866	3/1969	Lombard et al.	264—182

DONALD J. ARNOLD, Primary Examiner

J. H. WOO, Assistant Examiner

U.S. Cl. X.R.

8—149.3; 264—182, 210

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,514,512 Dated May 26, 1970

Inventor(s) Shigeru Kikuchi et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7, line 19: change "claim 8" to --claim 7--;

Column 8, line 4: after "claim" insert --1--.

SIGNED AND
SEALED
DEC 15 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334