(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 074 414**
B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **06.05.87**

(51) Int. Cl.⁴: **D 01 F 1/06**, D 01 D 1/00, D 01 D 5/06

(21) Application number: **81107025.9**

(22) Date of filing: **07.09.81**

(54) Method for preparing spin-dyed acrylonitrile polymer filaments.

(43) Date of publication of application:
23.03.83 Bulletin 83/12

(45) Publication of the grant of the patent:
06.05.87 Bulletin 87/19

(84) Designated Contracting States:
DE FR GB IT NL

(56) References cited:
FR-A-1 154 696
GB-A-1 383 317
US-A-2 039 708
US-A-2 972 546

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EP 0 074 414 B1

Description

The present invention relates to an improved method for preparing spin-dyed acrylonitrile polymer filaments from a colorant containing spinning solution, more particularly to an improved spinning method which permits the production of solution-dyed filaments in small lots.

GB—A—1 504 796 discloses a process for the spin dying of an acid-modified acrylonitrile homopolymer or copolymer. A particular basic dyestuff may be incorporated in the spinning solution by mixing a solution of the dyestuff with a solution of the polymer or by dissolving the polymer in a solution of the dyestuff. The mixture can then be homogenized and spun in the usual way—for example, according to the wet spinning process—but preferably it is spun according to the dry spinning process.

FR—A—1 154 696 (US—A—2 941 970) discloses a process for producing uniformly colored fibers from acrylonitrile polymers. Pigments are uniformly dispersed throughout solutions used in spinning fibers from said polymers. A water-dispersion of a pigment with a selected organic solvent (a color concentrate) is incorporated in solutions of acrylonitrile polymers, and fibres are prepared therefrom.

Hitherto, solution dyeing has been uneconomical for small-scale production because color change causes a loss of spinning solution and operating time.

The conventional solution-dyeing spinning method has been advantageous in that a small number of mixers are required because the spinning solution and the colorant are mixed in a process, e.g., spinning tank, which precedes the spinning metering pump. However, it is very difficult to clean a colored viscous spinning solution. Complete cleaning requires the disassembly of piping, filter, spinning solution feed pump, and metering pump. Color change in daily operation is carried out without such complete cleaning, and mixing of the previous color and the new color can easily happen, making color matching more difficult. Stopping the spinning machine for a long time for complete cleaning is quite uneconomical in small-lot production and is feasible only in the case where colored fibers of the same color are produced in a large quantity. The conventional method cannot meet economically the market requirements for filaments of different colors mixed together rather than filaments of a single color.

After extensive studies to solve these problems, the present invention has been completed.

It is an object of the present invention to provide an improved method for preparing spin-dyed acrylonitrile polymer filaments which permits the continuous production of solution-dyed filaments and tows in small lots and to obtain filaments of any desired color simply by changing the colorant to be added to the spinning solution and minimizing losses of colorant spinning solution. It is another object of the present invention to provide a method for spinning tows or filaments of a single color or filaments of different colors for each spinneret.

Accordingly, the present invention relates to a method for preparing spin-dyed acrylonitrile polymer filaments from a colorant-containing spinning solution which comprises injecting a colorant in a solvent which does not coagulate or precipitate the polymer, into a spinning solution in a nozzle holder in which a mixer and a spinneret are integrated by linking the two or arranging the mixer on the line just before the nozzle, whereby the colorant is uniformly mixed with the spinning solution and in a mixing ratio of spinning solution to colorant solution of 5:1 to 100:1 by volume.

More particularly the colorant solution is injected in a predetermined ratio into a passage between the spinning metering pump and the spinneret by the metering feed pump which interlocks with the spinning metering pump. The colorant solution is mixed with the spinning solution in a nozzle holder in which a mixer and a spinneret are integrated by linking the two or arranging the mixer on the line just before the nozzle. Thus, spin-dyed filaments or tows containing colorants are obtained.

The nozzle holder is of a structure such that the spinning solution and colorant liquid are mixed and passed as a piston-like flow without hold-up and need not be replaced when a color change is required. Thus, the method of the present invention permits one to obtain filaments of any desired color simply by changing the colorant to be injected.

The polymers to which the method of this invention is applied are acrylonitrile homopolymers and copolymers, preferably acrylonitrile polymers and modacrylic polymers having acid groups (such as carboxylic acid and sulfonic acid groups) in an amount of 10 to 100 mg equivalent/kg fiber. Such acrylonitrile polymers may contain 0 to 10 wt% of methyl methacrylate, methyl acrylate, and/or vinyl acetate, or up to 60 wt%, preferably not less than 10 wt%, of vinyl chloride and/or vinylidene chloride.

The colorants which can be used in the method of this invention include common cationic dyes, disperse dyes, and acid dyes, and metal complex dyes soluble in organic solvents. These dyes are used in the form of solutions in ethylene glycol, acetic acid, water, etc. or dispersions having a particle size of less than 0.1 μm. Those dyes which have high affinity for polymers are preferable from the standpoint of spinning and color fastness. Cationic dyes should preferably be combined with acrylonitrile polymers or modacrylic polymers. Such a combination results in less dissolution of dyes in the spinning bath and provides colored filaments having good color development and color fastness.

What is to be noted in the coloring by injecting colorants into the spinning solution in the spinneret or immediately before the spinneret is the mixing ratio and viscosity of the dope and colorant solution. The mixing ratio of spinning solution to colorant solution is 5:1 to 100:1 by volume. If the colorant solution is mixed in more than the upper limit of this ratio, the viscosity of the spinning solution decreases to such an extent that spinning is difficult to perform, and if the colorant solution is mixed in less than the lower limit

of this ratio, the color density cannot be increased and color shading can easily happen. The spinning solution should preferably have a viscosity from 0.5 to 50 Pas at 25°C for uniform mixing.

According to the method of this invention, it is possible to minimize losses of colored spinning solution resulting from color change which has been a serious drawback in solution-dyeing spinning, and to improve greatly the operating rate of the spinning machine for the production of a variety of filaments of different colors in small quantities. The method of the present invention can be applied to the known conventional spinning methods. From the standpoint of uniform coloring it is more suited to wet spinning which employs acetone, DMF, DMSO, ammonium thiocyanate, nitric acid, zinc chloride, etc. as a solvent for preparing the spinning solution.

In addition, the method of the present invention makes it easy to provide solution-dyed tows of different colors from individual spinnerets, instead of mixing filaments of different colors in order to obtain a deep color tone. This eliminates the blending of filaments and makes it possible to change color easily for each spinning and to provide desired color arrangements of deep tone.

The present invention will be described in detail with reference to the examples that follow. In the examples parts or percent means by weight unless otherwise specified.

Example 1

A spinning solution containing 25% polymer, and having a viscosity of 5 Pas at 25°C, was prepared by dissolving in acetone a copolymer consisting of 48 parts by weight of acrylonitrile, 51.2 parts by weight of vinyl chloride, and 0.8 parts by weight of sodium methallylsulfonate (sulfonic acid group in an amount of 50.7 mg equivalent/kg copolymer). A 7.5% coloring solution was prepared by diluting with acetone Cathilon® Yellow RLH liquid, (aqueous solution of a cationic dye; made by Hodogaya Chemical Co., Ltd.). The spinning solution was supplied by a gear pump at a rate of 200 ml/min, and the coloring solution was supplied by a constant rate pump at a rate of 20 ml/min. The mixing of the spinning solution and coloring solution was accomplished in a mixing unit installed immediately before the nozzle holder. The colored spinning solution was extruded from a spinneret having 6000 holes, each having a diameter of 0.08 mm, followed by coagulation in an acetone/water coagulating bath. The colored, extruded filaments underwent drying, drawing, and heat treatment so that the final fineness of a single filament was 3 denier (0.33 tex) and the fineness of the tow was 18000 denier (2000 tex). Nonuniformity of coloring was not observed in the resulting colored tow, and the coloring concentration was 3% o.w.f..

Example 2

Three kinds of tows colored in yellow, red, and blue were prepared as in Example 1 by switching the colorants in the order of A, B, and C as shown in Table 1.

TABLE 1

Names of dyes	Dye in dope (%)	Dye (% o.w.f.)	Time required for switching
(A) Cathilon® Yellow RLH liquid	7.0	2.0	A to B, 5 min.
(B) Cathilon® Red T-BLH liquid	0.7	0.2	B to C, 2 min.
(C) Cathilon® Blue T-BLH liquid	7.0	2.0	

It is to be noted that complete color change took only 5 minutes from a coloring concentration as high as 2% o.w.f. to a coloring concentration as low as 0.2% o.w.f., and switching from a low concentration to a high concentration took only 2 minutes.

Example 3

A spinning solution containing 23% polymer, and having a viscosity of 20 Pas at 25°C, was prepared by dissolving in dimethylformamide a copolymer consisting of 93.0 parts by weight of acrylonitrile, 5.9 parts by weight of vinyl acetate, and 1.1 parts by weight of sodium methallylsulfonate (sulfonic acid groups in an amount of 69.7 mg equivalent/kg copolymer). A 8.0% coloring solution was prepared by diluting Basacryl® Red GL (liquid, made by BASF) with dimethylformamide. The spinning solution was supplied by a gear pump at a rate of 200 ml/min, and the coloring solution was supplied at a rate of 15 ml/min. The mixing of the spinning solution and coloring solution was accomplished in a mixing unit installed immediately before the nozzle holder. The colored spinning solution was extruded from a spinneret having 6000 holes, each having a diameter of 0.08 mm, followed by coagulation and 400% drawing in a dimethylformamide/water coagulating bath. The colored filaments underwent drying and heat treatment so that the final fineness of single filament was 3 denier (0.33 tex) and the fineness of the tow was 18000 denier (2000 tex).

Nonuniformity of coloring was not observed in the resulting colored tow, and the coloring concentration was 2.5% o.w.f.. No contamination occurred in the spinning bath.

Example 4

A spinning solution containing 22.5% polymer was prepared by dissolving in dimethylformamide a copolymer consisting of 95% acrylonitrile and 5% methyl acrylate. A 5% coloring solution was prepared by diluting with dimethylformamide Spilon® Blue GNH (made by Hodogaya Chemical Co., Ltd.). Colored tows were prepared from the spinning solution and coloring solution as in Example 3 using a dimethylformamide/water coagulating bath.

The resulting colored tows have a deep color tone which is characteristic for metal complex dyes and different from the bright color tone obtained by dyeing acrylic fibers with a cationic dye. Also, the resulting tows exhibited good lightfastness, class 6, which is one of the characteristics of metal complex dyes.

Claims

1. A method for preparing spin-dyed acrylonitrile polymer filaments from a colorant containing spinning solution, which comprises injecting a colorant in a solvent which does not coagulate or precipitate the polymer, into a spinning solution in a nozzle holder in which a mixer and a spinneret are integrated by linking the two or arranging the mixer on the line just before the nozzle, whereby the colorant is uniformly mixed with the spinning solution and in a mixing ratio of spinning solution to colorant solution of 5:1 to 100:1 by volume.

2. A method as claimed in Claim 1, in which at least two spinnerets are used for the same spinning solution and different colorants are injected for respective spinnerets, whereby tows containing dyed filaments of different colors are obtained from the same spinning solution.

3. A method as claimed in Claim 1 or 2 in which the colorant is a dye.

4. A method as claimed in Claim 1 or 2 in which the colorant is a cationic dye.

5. A method as claimed in Claim 1 or 2 in which the polymer is an acrylonitrile polymer or copolymer having acid groups.

Patentansprüche

1. Verfahren zur Herstellung von in der Spinnflüssigkeit gefärbten Fäden aus Acrylnitril-Polymerisaten aus einer ein farbgebendes Mittel enthaltenden Spinnlösung, dadurch gekennzeichnet, daß man das farbgebende Mittel in einem Lösungsmittel, das das Polymerisat weder koaguliert noch ausfällt, in eine Spinnlösung in einem Düsenhalter injiziert, in dem ein Mischer und eine Spinndüse durch Verbinden der beiden oder durch Anordnen des Mischers in der Leitung unmittelbar vor der Spinndüse integriert sind, wodurch das farbgebende Mittel gleichmäßig mit der Spinnlösung und in einem Mischungs-Volumenverhältnis von Spinnlösung zu Lösung des farbgebenden Mittels von 5:1 bis 100:1 vermischt wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß mindestens zwei Spinndüsen für die gleiche Spinnlösung verwendet und verschiedene farbgebende Mittel für die jeweiligen Spinndüsen injiziert werden, wobei Fadenkabel mit gefärbten Fäden unterschiedlicher Fabre aus der gleichen Spinnlösung erhalten werden.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das farbgebende Mittel ein Farbstoff ist.

4. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das farbgebende Mittel ein Kationischer Farbstoff ist.

5. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Polymerisat ein saure Gruppen aufweisendes Acrylnitril-Polymerisat oder -Copolymerisat ist.

Revendications

1. Un procédé pour la préparation de filaments de polymère d'acrylonitrile teints dans la masse à partir d'une solution de filage contenant une matières colorante qui comprend l'injection d'un colorant dans un solvant, qui ne coagule ni ne précipité le polymère, dans une solution de filage dans un porte-buse dans lequel un mélangeur et une filière sont intégrés par réunion de ces deux derniers ou par disposition du mélangeur sur le trajet juste avant la buse, si bien que la matière colorante est mélangée uniformément à la solution de filage et dans un rapport de mélange de la solution de filage à la solution de matière colorante de 5/1 à 100/1 en volume.

2. Un procédé comme revendiqué dans la revendication 1 dans lequel au moins deux filières sont utilisées pour la même solution de filage et des matières colorantes différentes sont injectées pour les filières respectives, si bien que l'on obtient à partir de la même solution de filage des câbles contenant des filaments teints de couleurs différentes.

3. Un procédé comme revendiqué dans la revendication 1 ou 2 dans lequel la matière colorante est un colorant.

4. Un procédé comme revendiqué dans la revendication 1 ou 2 dans lequel la matière colorante est un colorant cationique.

5. Un procédé comme revendiqué dans la revendication 1 ou 2 dans lequel le polymère est un polymère ou un copolymère d'acrylonitrile ayant des groupes acides.