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

(11) Publication number: **0 241 054 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **87200306.6**

(22) Date of filing: **23.02.87**

(51) Int. Cl.4: **D01F 6/18** , D01D 10/00 , D01F 11/06 , D06P 3/76

(30) Priority: **07.03.86 IT 1966886**

(43) Date of publication of application: **14.10.87 Bulletin 87/42**

(84) Designated Contracting States: **AT BE CH DE ES FR GB GR LI LU NL SE**

(71) Applicant: **ENICHEM FIBRE S.p.A.**
Via Ruggiero Settimo 55
I-90139 Palermo(IT)

(72) Inventor: **Cognigni, Franco**
Via Cupello 3/A
I-20097 San Donato Milanese Milan(IT)
Inventor: **Sciolla, Ettore**
Vicolo Garibaldi 1§Fordongianus
I-09025 Oristano(IT)

(74) Representative: **Roggero, Sergio et al**
Ing. Barzanò & Zanardo Milano S.p.A. Via Borgonuovo 10
I-20121 Milano(IT)

(54) Improvements in methods for producing in-line dyed acrylic fibres.

(57) In the preparation of in-line dyed acrylic fibres by the wet-spinning process in which a solution of an acrylonitrile polymer in an organic solvent is extruded into a coagulum bath and the coagulated fibre is subjected to stretching and dyeing, a retraction step conducted under particular conditions is interposed between the stretching step and dyeing step, in order to improve the fibre dyeing characteristics.

EP 0 241 054 A2

IMPROVEMENTS IN METHODS FOR PRODUCING IN-LINE DYED ACRYLIC FIBRES

This invention relates to improvements in methods for producing in-line dyed acrylic fibres, in which dyeing is implemented during a stage of the wet-spinning process.

It is known in the art to prepare acrylic fibres by the wet-spinning process, which basically comprises:

-preparing a solution of an acrylonitrile polymer in an organic solvent (spinning dope);

-extruding said spinning dope through the holes of a spinneret and into a coagulum bath to form a fibre;

-stretching, washing and dyeing said fibre.

Dyeing an acrylic fibre during the spinning process falls within the known art, and its implementation depends on the particular morphology imposed on the fibre during spinning, this being desirably that of a finely distributed microporous structure. When such a structure of high unit surface area is imposed, the fibre is well suited for absorbing dyestuff solutions within a short time period such as to enable dyeing to be conducted continuously during the fibre production process itself, so avoiding the use of dyeing tanks of unusual dimensions.

Continuous acrylic fibre dyeing during the step preceding final drying of the produced fibre is described for example in French patent No. 2,538,823, in which dyeing is implemented immediately after the stretching step.

Methods are also known in which fibre dyeing is implemented before the stretching step.

In both cases there are technical problems, seemingly related to the manner in which the dyestuff solution is absorbed by the fibre, which can prejudice the proper progress of the dyeing operation.

In this respect, if dyeing is carried out before stretching, problems of dyeing uniformity arise deriving from the difficulty of attaining homogenous penetration of the dyestuff solution into a very voluminous fibrous mass.

The colour tonality thus frequently varies according to the position of the filaments in the fibrous mass, the most outer fibres being more intensely and uniformly coloured than the inner fibres.

Consequently, in order to obtain fibres of constant uniform colour tonality, use is generally made of sophisticated equipment arranged to keep the individual filaments spaced apart so as to allow easier contact with the dyestuff solution, or alternatively the time of contact between the acrylic fibre and dyeing bath is prolonged either by lengthening the dyeing tanks or by reducing the rate at which the fibre moves through the bath.

In all cases, these represent costly expedients.

Where dyeing is implemented after stretching, the increased ease of contact between the fibres and dyestuff solution deriving from the smaller unit volume of the fibrous mass is opposed by a lower fibre porosity, with consequent reduction in the capacity of the fibre to absorb adequate dyestuff quantities within short time periods.

The effects of this drawback are more evident when producing acrylic fibres dyed with very dark colour tones, which are therefore difficult to obtain.

It has now been found that the aforesaid drawbacks of the known art can be obviated or at least substantially reduced if during the wet-spinning process the acrylic fibre is subjected to special retraction treatment between the fibre stretching step and dyeing step.

In accordance therewith, the present invention provides for the preparation of dyed acrylic fibres by the wet-spinning process in which a solution of acrylonitrile polymer in an organic solvent is extruded into a coagulum bath and the coagulated fibre is subjected to stretching and dyeing, said process being characterised in that between the stretching step and dyeing step there is interposed a stretched fibre retraction step, said retraction step being conducted at high temperature in an aqueous-organic solvent.

In practice, in the retraction step the stretched fibre is brought into contact with an aqueous solution of the organic solvent used for the polymer at a temperature of between 100 and 120°C, so as to induce an extent of retraction generally varying from 25 to 40%, and preferably in the 30 to 38% range.

It has been found that when operating in the aforesaid manner, the acrylic fibre attains an unexpectedly high dyeing capacity, so that is becomes simple to obtain fibres dyed with dark tones, even with relatively low dyestuff concentrations of the order of 20-30 g/l in the relative bath, and with short dyeing times generally of the order of 1-5 seconds. In this manner, an economical advantage is also attained deriving from the reduced dimensions of the dyeing modules.

Suitable acrylonitrile polymers for the purposes of the present invention are products of the copolymerisation of acrylonitrile with 5-10% by weight of a monomer generally chosen from methyl acrylate, methyl methacrylate and vinyl acetate. Particularly preferred are those acrylonitrile

copolymers containing about 8% by weight of vinyl acetate. Conveniently, said acrylonitrile polymers have a means viscometric molecular weight of the order of 100,000-150,000.

Said polymers are dissolved in a highly polar, aprotic organic solvent generally chosen from dimethylformamide, dimethylacetamide and dimethylsulphoxide, to form a solution (spinning dope) containing 10-30% by weight of polymer. Preferably, the solvent is dimethylacetamide and the spinning dope contains 20-28% by weight of polymer.

The spinning dope obtained in this manner is degassed and filtered, and by means of a metering pump is then extruded through a spinneret into a coagulum bath.

Spinnerets suitable for this purpose can contain 1,000-60,000 holes having a diameter of between 40 and 150 microns.

The coagulum bath is a bath which does not dissolve the polymer but is able to extract the solvent from the spinning dope when this emerges from the spinneret holes.

Generally, the coagulum bath consists of an aqueous solution of dimethylformamide, dimethylacetamide or dimethylsulphoxide, the preference being for the actual solvent used in preparing the spinning dope.

Generally, the coagulum bath contains an organic solvent quantity of the order of 30-80% by weight, the operating temperature conveniently being 10°-60°C.

Coagulation takes place under these conditions, with the formation of filaments which after leaving the coagulum bath can be grouped to form a tow of the desired grade.

The coagulated fibre is then subjected to the usual stretching, to an extent generally within the 1:5 to 1:10 draft ratio range in the axial direction, and preferably of the order of 1:6-1:8. In the method of the present invention, the stretched fibre is subjected to retraction treatment to obtain a degree of retraction of between 25 to 40% and preferably of the order of 30-38%. This treatment is preferably conducted in an aqueous solution of dimethylformamide, dimethylacetamide or dimethylsulphoxide containing generally between 10 and 80% by weight of organic solvent and kept at a temperature of between 100 and 120°C.

In the preferred embodiment, an aqueous solution is used containing about 60-65% by weight of dimethylacetamide, the operating temperature being of the order of 105-110°C.

The retracted fibre is subjected to washing, which is conducted in countercurrent with demineralised water at a temperature of 80-100°C and preferably of the order of 90°C, to remove the residual solvent from the fibre.

According to the present invention, the washed fibre is dyed in dyeing baths containing a dyestuff or a mixture of several dyestuffs, in the form of an aqueous solution the concentration of which depends on the tonality to be obtained, and which for the darkest tones can reach values of the order of 30 g/l. Dyestuffs suitable for the purpose are cationic dyestuffs such as those of the azomethinic or azo type, or of the triphenylmethane class.

Specific examples of dyestuffs are those known commercially as C.I. Basic Yellow, C.I. Basic Violet, C.I. Basic Red, C.I. Basic Blue and C.I. Basic Orange.

The aqueous dyeing bath conveniently has a pH of the order of 3-5, the operating temperature being between 30 and 80°C, with contact times of between 1 and 5 seconds.

For this purpose, dyeing tanks are generally used fitted with homogenising paddles and circulating pumps, the former moving at a speed of between 1 and 2 times the fibre speed, so as to subject the fibre to between 20 and 40 oscillations/sec/m. After dyeing, the fibre is wrung, and treated thermally with saturated steam at 100°C for about 10 seconds to complete dye fixing. The usual steps of washing to remove non-fixed dyestuff, lubrication with a solution of non-ionogenic products, drying and crimping then follow.

The following experimental examples illustrate the scope of the invention but are not meant to limit it.

EXAMPLE 1

Acrylic fibre is wet-spun in an industrial spinning line, with an hourly fibre production of 800 kg at a final rate of 50 m/min. Specifically, a copolymer is used for this purpose containing 92% by weight of acrylonitrile and 8% by weight of vinyl acetate, and with a specific viscosity of 0.145 l/g.

A solution containing 26% of the copolymer in dimethylacetamide is prepared. After degassing and filtering, this spinning dope is fed into a coagulum bath through spinnerets with 52 micron diameter holes.

The coagulum bath, in the form of an aqueous solution containing about 55% by weight of dimethylacetamide, is kept at 50°C and the formed filaments are grouped into various tows.

The fibre is then stretched to a draft ratio of 1:6 in the axial direction, and is then subjected to retraction. This latter operation is conducted continuously in an aqueous bath containing 62% by weight of dimethylacetamide and kept at a temperature of about 106°C. Under these conditions, a retraction of 30% is obtained.

After the retraction step the fibre is washed countercurrently at 90°C with demineralised water, and is then dyed continuously in a dyeing module consisting of a tank of about 2 metres in length fitted with two homogenising paddles each comprising six bars, and with a circulation pump.

The fibre rate through the dyeing module is about 50 m/minute, and the dyeing time (defined as the time of contact of the fibre with the dyestuff solution) is 2.4 seconds, the paddle speed being 80 m/minute.

Specifically, the dyeing bath is kept at 70°C and comprises a 25g/l concentration of a dyestuff mixture consisting of C.I. Basic Yellow 28 (42% by weight), C.I. Basic Red 49 (14% by weight) and C.I. Basic Blue 41 (41% by weight).

The dyestuff make-up feed into the dyeing tank is 40 l/hour, corresponding to 5% by weight of the fibre.

After dyeing, the tows are wrung, treated thermally with saturated steam at 100°C for about 10 seconds in order to fix the dyestuff, washed in order to remove non-fixed dyestuff, lubricated with a solution of non-ionogenic products, dried, crimped and collected.

Under these conditions an intensely and homogenously black-dyed fibre is obtained containing about 5% by weight of dyestuff, this percentage relating to the liquid form of the commercial dyestuff used.

The fibre also has the following characteristics:
Count: 3.3 dtex
Toughness: 25.4 CN/tex
Ultimate elongation: 40.5%
Shrinkage in water at 100°C: 2.5%
Lubrication: 0.5%

EXAMPLE 2 (comparison)

The procedure of Example 1 is followed but omitting the retraction step. In this case the instantaneous maximum dyestuff quantity contained in the fibre is 3.12% by weight, the percentage again referring to the liquid form of the commercial dyestuff used. Consequently, the fibre colour is distinctly lighter than that of the fibre of Example 1. Only when the dyeing bath concentration reaches 40 g/1 is a fibre obtained of colour equal to that of Example 1.

It will be noted from the aforegoing examples that if the dyeing constant (K dye.) is expressed as the ratio of the quantity of dyestuff on the fibre (expressed as percentage by weight) to the dyestuff concentration in the dyeing bath (expressed as g/l), the following results are obtained:
K dye. of Example 1 = 5/25 = 0.20
K dye. of Example 2 = 5/40 = 0.125
for equal fibre coloration in the two examples.

The values indicate that when the dyeing bath is changed, 12.5 kg of dyestuff are lost in the case of the first example, whereas 20 kg of dyestuff are lost in the case of the second, example, for a typical bath of 500 litres.

Claims

1. A method for preparing acrylic fibres by wet-spinning, in which a solution of an acrylonitrile polymer in an organic solvent is extruded into a coagulum bath and the coagulated fibre is subjected to stretching and dyeing, characterised in that between the stretching step and dyeing step there is interposed a stretched fibre retraction step, said retraction step being conducted at high temperature in an aqueous-organic solvent.

2. A method as claimed in claim 1, characterised in that the retraction step is conducted by bringing the stretched fibre into contact with an aqueous solution of the polymer organic solvent at an operating temperature of between 100 and 120°C and preferably between 105 and 110°C, to induce a retraction of between 25 and 40% preferably between 30 and 38%.

3. A method as claimed in claim 2, characterised in that said aqueous solution of the polymer organic solvent is an aqueous solution containing between 10 and 80% by weight of dimethylformamide, dimethylacetamide or dimethylsulphoxide.

4. A method as claimed in claim 2, characterised in that said aqeuous solution of the polymer organic solvent is an aqueous solution containing 60-65% by weight of dimethylacetamide.

5. A method as claimed in claim 1, characterised in that said retracted fibre dyeing step is conducted by contact with an aqueous solution containing up to 30 g/l of a cationic dyestuff or a mixture of cationic dyestuffs, at a temperature of between 30 and 80°C for a contact time of between 1 and 5 seconds.

6. A method as claimed in claim 1, characterised by subjecting the fibre to a water wash between the retraction step and dyeing step.

7. A method as claimed in claim 6, characterised in that said wash is conducted countercurrently with demineralised water at a temperature of about 80-100°C.