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(71) Applicant: **MONTEFIBRE S.p.A.**
I-20124 Milano (IT)

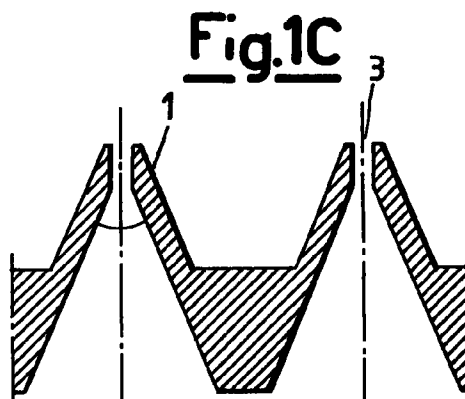
(72) Inventors:
• **Busato, Giampaolo**
30174 Mestre Venezia (IT)

• **Signoretti, Luigi**
30173 Venezia (IT)
• **Tedesco, Raffaele**
30171 Mestre Venezia (IT)

(74) Representative: **Fusina, Gerolamo et al**
Ing. Barzanò & Zanardo Milano S.p.A.
Via Borgonuovo, 10
20121 Milano (IT)

(54) **Acrylic fibre production process using a novel type of spinnerette head**

(57) A process for producing acrylic fibre by a dry extrusion/wet coagulation technique is disclosed which uses a spinnerette with a particular geometry of the extrusion surface.



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Description

The present invention relates to a method for producing acrylic fibre from a polymer solution by using the so-said "dry-jet wet spinning".

When fibres are produced from polymer solutions, the solution leaving spinnerette capillaries is known to undergo a swelling due to the elastic recovery of the strain undergone by the polymer solution. This effect is also known as "Barus effect".

This filament swelling may reach values, expressed as the ratio of the diameter of the extruded filament to the diameter of the capillary bore, which are comprised within the range of from 3 to 4, and may even be higher than that.

In the traditional wet spinning, in which the spinnerette is directly dipped inside the coagulation bath, a nearly instantaneous surface hardening takes place in the filament as soon as the latter emerges from the spinnerette bore, which contributes to limit the spontaneous expansion of the solution. Unfortunately, this effect is associated with some drawbacks, i.e.: poor plasticity of the filament with the stretching ability or thinning factor in the spinnerette being consequently limited; and presence of remarkable streaks on end fibre side surface.

The limited spinning stretching ability limits the possibility of producing fibres with a lower count than 0.7 dtex even if thin-diameter capillaries are used, e.g., of 35 microns.

The presence of surface streaks leads to fibres with poor gloss values owing to the irregular light reflection and an increased roughness of the hand with which the finished articles are felt, owing to the resulting increase in friction coefficient. The higher the ratio of the diameter at the coagulation step to the end fibre diameter, the more the side surface of the end fibre will be affected by streaks.

The spinning technique of "dry-jet wet spinning" (DJWS) according to which filament spinning takes place under dry extrusion conditions and subsequent wet coagulation, allows the above drawbacks to be overcome. In fact, when it emerges from the bores, the filament is still in fluid phase and, consequently, its still sufficiently plastic condition enables it to withstand even high spinning stretching ratios and the end fibre to retain an extremely smooth side surface, free from longitudinal streaks.

Unfortunately, also DJWS spinning, which, from a theoretical point of view, makes it possible fibres to be produced with high extrusion rates and with particularly smooth surfaces, suffers from drawbacks.

The most important drawback is the swelling undergone by the polymer solution on emerging from spinnerette capillaries, on the spinnerette surface, which may cause the individual filaments to get fused with the filaments exiting the adjacent capillaries, owing to the swelling being no longer limited by the solidification of the coagulated surface. Usually, in order to overcome

this drawback, the distance between the spinnerette bores is increased. Unfortunately, even under these conditions, spinning is unstable owing to the sudden breakage of the filaments.

As a consequence of the above drawbacks, the spinnerette productivity allowed by the DJWS technology is low owing to the small number of bores which can be provided through the spinnerette in order to prevent the filaments from getting fused with one another and the poor spinning stability with consequent frequent spinning interruptions.

The present Applicant has now surprisingly overcome these problems and drawbacks by using a dry extrusion/wet coagulation spinning method by using a spinnerette which, while retaining the typical diameter of the customarily used spinnerettes, has a larger extrusion surface area and a larger number of capillary bores.

In accordance therewith, the purpose of the present invention is a process for producing fibres from soluble, spinnable polymers, performed by means of the following operating steps:

(a) extruding continuous filaments of polymer solution by means of a spinnerette comprising

- a spinnerette body,
- a spinnerette head of circular shape, containing a plurality of bores with a diameter comprised within the range of from 75 to 600 microns, provided parallelly to the diameter, with these bores being furthermore provided on protruding portions, having a defined geometry, extending from the surface of said spinnerette head;

(b) stretching the continuous filaments inside a non-coagulant fluid;

(c) causing said continuous filaments to run through a coagulant liquid in order to form the polymer fibres.

The head of a typical spinnerette according to the present invention is disclosed now by referring to Figures 1A - 1B - 1C- 1D..

In Figure 1A, a plan view is shown which illustrates the bore distribution scheme; in Figure 1B a cross-sectional view of the spinnerette is shown, in which the protruding portions (1) are given a cone frustum shape; in Figure 1C a detail (2) of Figure 1B is shown, in which the cone-frustum shaped protruding portions (1) and the bores (3) on their top land are illustrated. The lead-in cone leading to the bores has an opening angle of 45°. The lead-in portion can be given a cylindrical shape.

The protruding portions provided on the spinnerette surface can be given, rather than a cone frustum shape as illustrated in Figure 1B, a hemispherical shape (4) as illustrated in the cross-sectional view of Figure 1D. The

geometry of the protruding portions can also be still different, e.g., said protruding portions can parallelepipedal or pyramid-frustum shaped.

The diameter of the bores can be comprised within the range of from 75 to 600 microns, according to the desired diameter for the extruded filament. The number of bores provided through the spinnerette head is a function of the number of filaments which the thread manufactures wishes to have in the roving and are spaced apart from each other by a distance comprised within the range of from 1 to 4 mm.

According to a different embodiment of the present invention, the bores through the spinnerette head are not provided at the protruding portions extending from the spinnerette surface, but at the valleys between protruding portions.

The process according to the present invention is disclosed now by referring to Figure 2.

The polymer is dissolved in a suitable solvent, as dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, or other known solvent means.

The polymer solution is fed (5) to the spinnerette block (6) and is dry-extruded at 35°C through a spinnerette (7) similar to the spinnerette disclosed hereinabove. The spinning stretch ratio V_1/V_0 , defined as the ratio of

- V_1 , the speed at which the roving is pulled by a first pair of rollers, as metres/minute (m/min), to
- V_0 , the theoretical surface speed of the polymer solution

$$V_0 = (4 \times Q / \eta \times D^2) \times 10^6 \text{ m/min}$$

(wherein Q is the flow rate of the solution relatively to the bore wall, as ml/min, D is the diameter of the spinnerette bore, as microns)

may have variable values, and is however at least 3 times as high as the usual spinning stretch ratio values which can be obtained in the traditional wet spinning processes.

After the dry span (under preferred conditions, air is used as the non-coagulant fluid; however, other gases can be used as well), the conical bundle (8) of filaments of polymer solution is then wet-coagulated by dipping it into a coagulant bath (9). The distance travelled by the filaments through the dry gap before entering the coagulant bath depends on various factors, and, in particular, on the diameter of the individual bores of the spinnerette, the number of filaments, the viscosity of the solution, and so forth. This distance is preferably comprised within the range of from 1 to 4 cm.

The coagulant liquid means can be any of the large number of aqueous mixtures of organic solvents known from the prior art.

The roving of coagulated filaments (10) is caused to run, and returned, around a metal rod (11) provided at the bottom of the coagulant bath and is then caused to run around a first pair of pulling rollers (12).

After being washed with hot demineralized water in order to remove most residual solvent, the filaments roving is submitted to a second stretch step by getting immersed in boiling water and is then caused to run around a second pair of rollers revolving with a peripheral speed V_2 . The ratio of V_2/V_1 is the preset stretch ratio.

After subsequent washing steps to remove all residual solvent, the roving enters a finishing bath to be impregnated with such additives as lubricants, antistatic agents and, if so required, softening agents.

After this finishing step, the roving is wound around a subsequent pair of heated rollers (which can be either electrically or steam heated) in order to dry the filaments and stabilize the structure thereof.

The roving leaves this treatment step with a temperature of about 150°C and is then cooled by being caused to run around water-cooled rollers running at the same speed of the preceding rollers.

The fibre can be collected on bobbins or, either plain or crimped, inside containers. If so required by the end use the fibre is designed for, the fibre can also be submitted to an autoclave treatment with saturated steam in order to enable the stresses supplied by the stretch to get released, decrease the fibre brittleness and supply the fibre with better dyeing properties.

The polymers to be used with the instant invention preferably are polyacrylonitrile and acrylonitrile copolymers.

By means of the present process which, according to the present invention, uses a particular spinnerette type with a large number of bores, a productivity is obtained which is comparable to productivity allowed by the traditional wet process with an outstandingly spinning stability, without filament breakages and spinning interruptions, and furthermore filaments are produced which display a smooth surface and good mechanical properties, good gloss, good dyeing properties, and the like.

The following examples are supplied in order to allow the invention to be better understood, and should not be construed as being limitative of the same invention.

Example 1

A solution is prepared of 93%/7% acrylonitrile/vinyl acetate copolymer with a specific viscosity of 0.155, with a ratio of solvent:polymer of 75:25 by weight, in such a way that the viscosity of the resulting solution is of 400 poises at 50°C.

The solution is extruded in air, at the temperature of 35°C, through a spinnerette installed 1 cm away from the coagulant bath. The spinnerette is provided with 800 protruding portions with cone frustum geometry spaced apart by 1 mm from each other. Through the top land of the protruding portions a same number of bores of 175 microns of diameter are provided.

The coagulant bath is constituted by an aqueous solution containing 60% dimethyl acetamide, kept at the temperature of 30°C. The solution is fed to the spinnerette with a flow rate of 145 ml/min. The pulling speed V_1 of the first roller pair is of 20 m/min, the speed V_2 of the second roller pair is of 150 m/min. The following stretch ratios are obtained: spinning stretch ratio V_1/V_0 of 2.75 and boiling water bath stretch ratio V_2/V_1 of 7.5.

The subsequent finishing, drying and collapsing steps take place at the speed of 150 m/min.

The roving, collected on a bobbin, has a total count of 232 tex, with the count of each individual filament being of 0.29 tex. Heat-setting of fibre takes place inside an autoclave with saturated steams under 3.3 bars.

When viewed under the microscope, the filaments display a very smooth surface, without streaks and with a kidney-shaped cross section.

The mechanical characteristics, as determined by means of the commonly known techniques in the art are listed in following Table 1.

Table 1

-- Count	dtex	3.65
-- Toughness	cN/tex	37.7
-- Elongation at break %		40.4
-- Elastic modulus	cN/tex	689

Example 2

(Comparison Example)

The same spinning solution as used in Example 1 is fed, with the same flow rate, to a traditional spinnerette having the same number of bores of same diameter, positioned at the same distance from a coagulant bath having the same composition and temperature as in Example 1.

The spinning process proves to be extremely critical; in fact, the following drawbacks occur:

(a) Spinning is difficultly started up with the spinnerette being positioned above the coagulant bath, because the spinning solution drips without originating individual filaments. The separation of individual filaments can only be obtained by dipping the spinnerette into the coagulant bath for a few seconds, and then raising the spinnerette up to the level of 1 cm above the coagulant bath.

(b) The spinning process is unstable owing to the complete breakage of the roving or due to solution dripping caused by filaments fusing with one another. These events occur with a so high frequency that meaningful fibre amounts for characterization cannot be collected.

Even reducing the number of bores to a half and therefore increasing the mutual bore distance does not make it possible the process to be improved.

Claims

1. Process for producing fibres from soluble, spinnable polymers, performed by means of the following operating steps:

(a) extruding continuous filaments of polymer solution by means of a spinnerette comprising

- a spinnerette body,
- a spinnerette head of circular shape, containing a plurality of bores with a diameter comprised within the range of from 75 to 600 microns, provided parallelly to the diameter,
- with these bores being furthermore provided on protruding portions, having a defined geometrical shape, extending from the surface of said spinnerette head;

(b) stretching the continuous filaments inside a non-coagulant fluid;

(c) causing said continuous filaments to run through a coagulant liquid bath in order to form the polymer fibres.

2. Process according to claim 1, characterized in that in the spinnerette head the bores are provided in the regions between the protruding portions.

3. Process according to claim 1, characterized in that the protruding portions provided on the spinnerette head have a geometrical cone frustum shape.

4. Process according to claim 1, characterized in that the protruding portions provided on the spinnerette head have a geometrical hemispherical shape.

5. Process according to claims 1 to 4, characterized in that the polymer in solution is an acrylonitrile/vinyl acetate copolymer.

6. Process according to claims 1 to 4, characterized in that the polymer in solution is polyacrylonitrile.

7. Spinnerette for implementing the process according to claims 1 to 6, comprising

- a spinnerette body,
- a spinnerette head of circular shape comprising a plurality of bores, each bore with a diameter comprised within the range of from 75 to 600 microns, provided parallelly to the diameter and at a distance of from 1 to 4 mm from one another,

characterized in that said bores are provided on protruding portions having a defined geometrical shape extending from the surface of said spinnerette head.

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8. Spinnerette according to claim 7, characterized in that in the spinnerette head the bores are provided in the regions between the protruding portions.

9. Spinnerette according to claim 7, characterized in that the protruding portions provided on the spinnerette head have a geometrical cone frustum shape.

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10. Spinnerette according to claim 7, characterized in that the protruding portions provided on the spinnerette head have a geometrical hemispherical shape.

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11. Spinnerette according to claim 7, characterized in that the bores provided through the spinnerette head are provided at a distance of 1 mm from one another.

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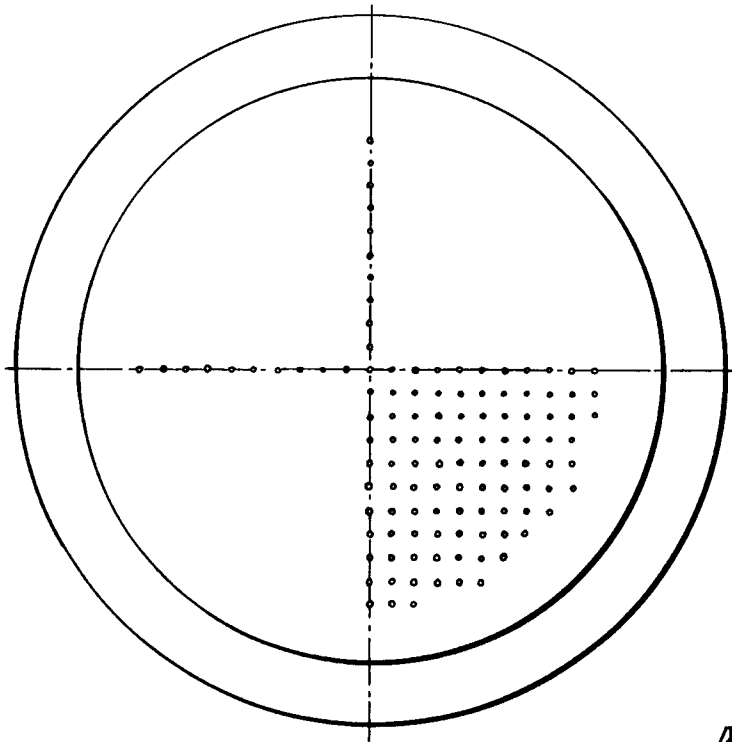


Fig.1A

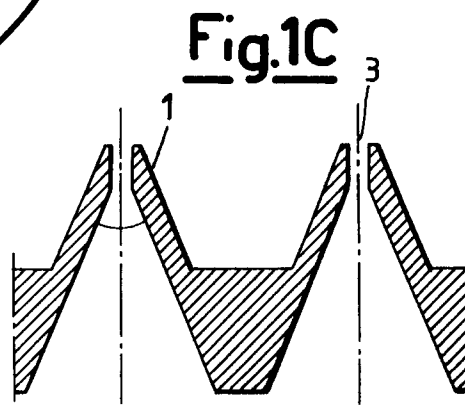


Fig.1C

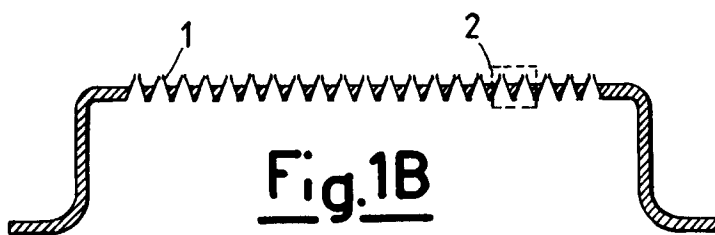


Fig.1B

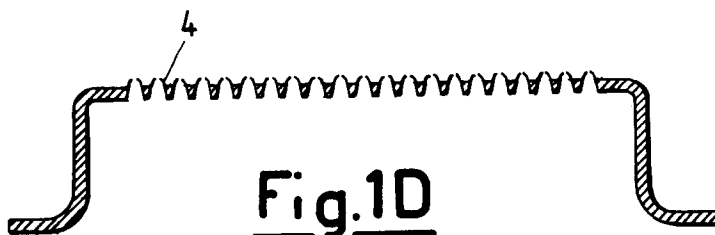


Fig.1D



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EUROPEAN SEARCH REPORT

Application Number
EP 96 20 0179

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Y	US-A-1 672 644 (H HOFFMANN ET AL) * the whole document * ---	1,3,5-7, 9,11	
Y	US-A-2 211 946 (G DE WITT GRAVES) * the whole document * ---	1,3,5-7, 9,11	
Y	PATENT ABSTRACTS OF JAPAN vol. 008, no. 106 (C-223), 18 May 1984 & JP-A-59 021709 (ASAHI KASEI KOGYO KK), 3 February 1984, * abstract * ---	1,3,5-7, 9,11	
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20 June 1996	Examiner Tarrida Torrell, J
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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Application Number
EP 96 20 0179

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
Place of search THE HAGUE		Date of completion of the search 20 June 1996	Examiner Tarrida Torrell, J
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