(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 December 2006 (14.12.2006)

PCT

(10) International Publication Number
WO 2006/131081 A1

(51) International Patent Classification:
D01D 5/00 (2006.01)

(21) International Application Number:
PCT/CZ2006/000037

(22) International Filing Date: 1 June 2006 (01.06.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PV2005-360 7 June 2005 (07.06.2005) CZ

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(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

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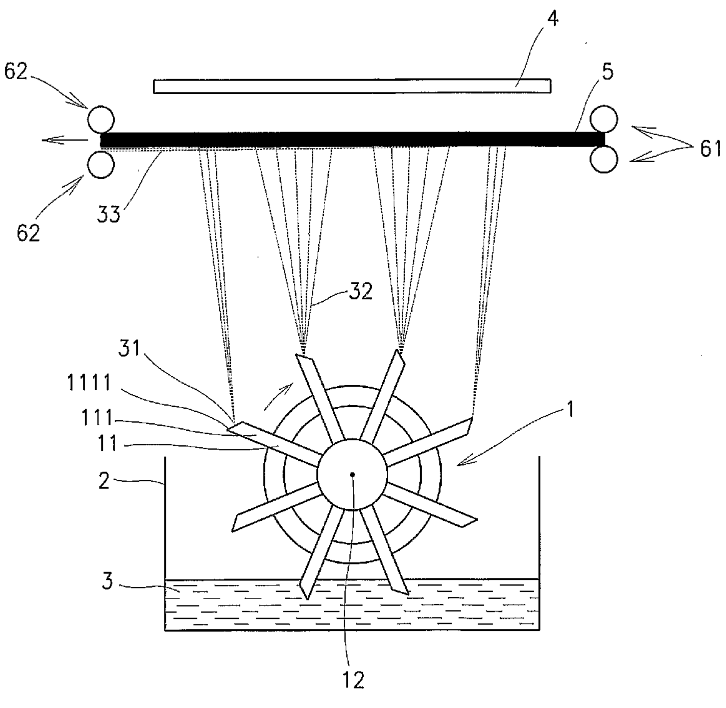
(54) Title: A METHOD AND DEVICE FOR PRODUCTION OF NANOFIBRES FROM THE POLYMERIC SOLUTION THROUGH ELECTROSTATIC SPINNING



(57) Abstract: Production method of nanofibres from the polymeric solution through electrostatic spinning in electric field created by a difference of potentials between the collecting electrode (4) and pivoted spinning electrode (1) of an oblong shape touching by a part of its circuit the polymeric solution (3), while by rotation of the spinning electrode (1) the polymeric solution (3), at least by a portion of its surface, is carried out into the electric field in which on the surface of the collecting electrode (4) the nanofibres are created which are carried to the collecting electrode (4) and deposited on the surface of a basic material (5) guided between the spinning electrode (1) and the collecting electrode (4) in vicinity of the collecting electrode (4). The polymeric solution (3), on surface of the spinning electrode (1) in a place of intersection of surface of the spinning electrode (1) with the plane interlaid by the axis of the spinning electrode (1) and being perpendicular to the plane of the base material (5), along the whole length of the spinning electrode (1), is subject to the electric field of a maximum and equal intensity, through which a high and even spinning effect is achieved along the whole length of the spinning electrode (1). The invention also relates to the device for production of nanofibres from polymeric solution through electrostatic spinning.

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— *with amended claims and statement*

A method and device for production of nanofibres from the polymeric solution through electrostatic spinning

Technical field

The invention relates to the production method of nanofibres from the polymeric solution through electrostatic spinning in electric field created by a difference of potentials between the collecting electrode and pivoted spinning electrode of an oblong shape touching by a part of its circuit the polymeric solution, while by rotation of the spinning electrode the polymeric solution, at least by a portion of its surface, is carried out into the electric field in which on the surface of the collecting electrode the nanofibres are created which are carried to the collecting electrode and deposited on the surface of a basic material guided between the spinning electrode and collecting electrode in vicinity of the collecting electrode.

The invention also relates to the device for production of nanofibres from polymeric solution through electrostatic spinning in electric field created by a difference of potentials between the collecting electrode and the pivoted spinning electrode of an oblong shape coupled with a drive and touching by at least a portion of its surface the polymeric solution with the objective to carry out the polymeric solution by these portions of surface into the electric field between the spinning electrode and the collecting electrode, while between the spinning electrode and the collecting electrode the track for passage of the basic material is created, the surface of which from the side of the spinning electrode serves for depositing of the nanofibres created.

Background art

The nanofibres are prepared from a broad range of polymers and polymer compounds, this either from the solutions using the solvents on the water or non-water basis. Various low-molecular additives may or need not to be added into the solutions as the need may be, which after then regulate some important physical properties of the solution being subject to spinning or which bring new chemical, physical, biological or other properties into the resultant polymer. At the same time the nanonfibres may be prepared also from the melts of polymers, but in contrast to the in principle similar processes of creating the polymeric melts, during processing of solutions smaller diameters of fibres are reached thanks to lower viscosity of solutions when compared with melts. For formation of solutions the mechanical forces of flowing gaseous media or the coulomb forces in electrostatic field are being used, so called electrostatic spinning, which leads to the fibres of smaller diameters.

The patents US 6 382 526 and US 6 520 425 represent an example of preparation of nanofibres from polymeric solution through a stream of air. The diameters of nanofibres produced by this technology are of 200 to 3000 nanometers.

The patent applications WO 0127365, WO 0250346, US 2002/0175449 A1, US 2002/084178 A1 and WO 2005/024101 A1 describe examples of preparation of nanofibres from polymeric solutions upon acting of electrostatic field of an average intensity of 50.000 to 500.000 V/m. The first four mentioned applications represent a solution which partially resembles the solution quoted in patents using the mechanical forces of gas stream. Again here are the jets of circular section and of inner diameter 0,5 to 1,5 mm), to which the voltage of direct current is applied. Opposite the jet from which the polymeric solution is forced out, mostly the grounded electrode (collecting electrode) is positioned. Such arrangement results in drawing of a thin further splitting beam of polymeric solution which finally provides the nanofibres. The greatest problem of this method is a low output. On one spinning jet, 0,1 to 1 gram of polymer in one hour may be , which, from the point of view of industrial usage, creates the production of nanofibres according to these solutions rather problematic. To the benefit of an output and also of homogeneity of the applied layer to the collecting electrode or to the ground, which is positioned between the jet and the collecting electrode in its vicinity, a group of static or moving jets can be built. Unfortunately the number of jets cannot be increased in an unlimited way, as well as there are limits as to the distance of jets among each other, which is given by the electric field itself, so also this solution does not bring a decisive point as regards an output. Next to this, here are further limits arising out of the general physical laws as the impossibility to increase the tension above the limit of a specific dielectric strength of air in the space of spinning, unsubstantiality of the proportional increasing of distance of electrodes, etc.

The GB 1 346 231 publishes a device for electrostatic spinning of polymer solutions containing the annular spinning electrode pivoted in a vertical plane by its lower part in polymeric solution and by its upper part between two vertically mounted collecting electrodes. The solution being subject to the spinning is carried out by the surface of a ring of the spinning electrode, at the same time the spinning process proceeds in the upper part of the annular spinning electrode positioned between the collecting electrodes in places, which are as much close as possible to these flat electrodes. The device can only hardly be used in industry as it is complicated, non-productive and the possible layer of fibres, eventually the non-woven textile produced by electrostatic spinning would be of a very irregular thickness and structure.

Next to this, the solution according to EP 1059106 A2 is known, which describes a device for change over of the solution or the polymer melt into the fibrous structure that contains a plane collecting electrode and a spinning electrode between which the electric field is created. The spinning electrode serves for transportation of the solution or of polymer melt (hereinafter referred to as solution only) into the electric field, simultaneously it is essential, that layers of polymer solution of a sufficiently high curvature are created on it on which the charge of electric field is concentrated so that the nanofibres are created from solution layer or from the melt. The nanofibres created are carried to the collecting electrode by action of the Coulomb forces. In one of the described variants, the spinning electrode is formed by a pivoted disc provided on its perimeter by protrusions, and the disc is dipped by a part of its perimeter into the polymer solution and brings the liquid polymer out into the electric field. The disc surface is wettable by a polymer solution so that this creates a coating on it. Once the disc rotates, each protrusion is gradually covered by a layer polymer solution, which gradually gains a charge of electrode, this means negative) and thanks to a high curvature the nanofibres are created on it. Polymer solution which has not been consumed returns back to the reservoir. The disc is positioned with the rotation axis parallel to the movement direction of the base fabric. The disadvantage of this solution is a small efficiency, because into the electrostatic field only a small quantity of polymer solution being subject to spinning penetrates and only a small portion is changed over into the fabrics. Another disadvantage is irregular thickness of nanofibre layers along the width.

Further there is depicted an askew mounting of a larger quantity of discs provided with protrusions on their perimeter, which may be positioned in a skew position towards the discharging electrode. According to the invention it is advantageous if the disc cores are of an isolation material to prevent effects superimposing the electric field. The solution should bring an advantage in a more even coating of fibre layer to the base material. The solution is very complicated due to the rotational drive of askew positioned discs and increasing of evenness of applied layer of nanofibres is possible only in the direction of movement of the base material and it cannot be presumed even in the direction of the width of the base material.

Other execution describes the discs illustrated in Fig. 14, on the perimeter of which the shaped protrusions are created and under those a collecting cavities for polymeric solution to facilitate dosing of quantity of polymeric solution and its advantage should consist in that the same quantity of polymeric solution is always repeatedly brought into the electrostatic field for spinning. The disadvantage of this solution is that the spinning takes place on the peaks of protrusions where concentration of the charge is the greatest while the collecting cavities are arranged on the smaller diameter than the peaks of protrusions, so it is complicated to transport the measured off quantity of a polymeric solution to the respective peak. Moreover upon rotation direction of a disc in the arrow direction illustrated in Fig. 14 by an arrow into the collecting cavities (151) no polymeric solution is taken, it would only be possible that the solution flows down into them which got stuck on surface of the protrusions at their rotation in the upwards direction. At the same time it is improbable, that always the same quantity of polymeric solution is dosed into the collecting cavities.

The technology shown in the WO 2005/024101 A1 patent tries to successfully solve the problem with output and other issues of the above mentioned solutions. In this case the spinning electrode is created of an electrode in the shape of a cylinder which rotates around its main axis and with its lower part of the surface is being dipped into the polymeric solution. The cylinder axis is positioned in the plane being parallel with a plane of a base material and perpendicular to the motion direction of the base material. On a surface of the cylinder a thin layer is being carried out from which at the simultaneous creation of so called Taylor cones the above mentioned beams of solution are being drawn which after then form on a collecting counter-electrode or on a suitable base layer, a layer of nanofibres in front of it. The mentioned technology works very good for polymeric solutions on a water basis. It does not solve the spinning issue for solutions on a non-water basis. This is connected with a basically different character of water and non-water solutions, which is first of all given by the presence of a strong dipole moment in a small water molecule. This predetermines totally different properties of water and non-water polymeric solutions from the point of view of effects of the outer electric field. Also at the water polymeric solutions the created layer of nanofibres is not totally even along the whole length of the spinning electrode.

From the above mentioned it is obvious that the principle of the up to now designed devices for preparation of quality nanofibres and layers of nanofibres is always a couple of electrodes on a different electrical potential. Without exaggeration the electrodes and their structure are the heart of the whole device and they predetermine by a decisive manner the success or failure of the whole device in production of nanofibres.

The objective of the invention is to create a method and a device which could be industrially usable also for spinning of polymeric solutions in solvents on the non-water basis and which would achieve a high spinning output and at the water and non-water solutions of polymers would further increase the evenness of created layer of nanofibres.

The principle of invention

The objective of the invention has been reached through a method of production of nanofibres from the polymeric solution by electrostatic spinning in electric field according to the invention whose principle consists in that the polymeric solution on surface of the spinning electrode in a place of intersection of surface of the spinning electrode with the plane interlaid by the axis of the spinning electrode and being perpendicular to the plane of the base material, along the whole length of the spinning electrode is subject to the electric field of a maximum and equal intensity, through which an equal and even spinning effect is achieved along the whole length of the spinning electrode, and as a result of it also the even thickness of nanofibre layer deposited on a base material.

It is advantageous, if the polymeric solution is brought into the electric field in quantities of same batches divided one from another that are moving around the circular tracks in the electric field while the mutual position of batches does not change and the batches are arranged in groups of batches, situated along the length of the spinning electrode in a plane running through the axis of the spinning electrode and perpendicular to the plane of base material with respect to the collecting electrode on the equipotent line of the highest intensity of electrical field between the spinning electrode and collecting electrode. Distribution of the polymeric solution into batches and positioning of each batch in the time when it is as close as possible to the collecting electrode in a place with highest intensity of electric filed.

The direction of carrying out the polymeric solution batches divided one from another is, with advantage, reverse towards the sense of base material movement through which the greater evenness of created nanofibre layer is achieved.

The principle of a device for production of nanofibres from polymeric solution through electrostatic spinning in electrical field consists in that the coating surface of sections of surface of the spinning electrode serving for carrying out the polymeric solution into the electric field is, in the plane running through the axis of the spinning electrode and perpendicular to the plane of the base material, of a shape created by the equipotent line of electric field between the spinning electrode and collecting electrode being of the highest intensity.

For spinning of the water polymeric solutions it is sufficient, if the coating surface is filled, which makes the structure of these devices easier.

For spinning of the water as well as the non-water polymeric solutions the spinning electrode contains a system of corrugated lamellas made of a flat electrically conductive material, which are towards the rotation axis mounted tangentially with their corrugation, at the same time in a plane perpendicular to the plane of the base material and running through the rotation axis of the spinning electrode and in the centre of the corrugated lamella they have a shape of equipotent line of the highest intensity of electric field between the spinning electrode and collecting electrode. Such spinning electrode is able to carry out a sufficient quantity of polymeric solution into the most suitable places of electric field between the spinning and collecting electrode, and simultaneously to perform a good spinning also of non-water polymeric solutions.

At the same time it is advantageous, especially for a quicker starting of spinning and maintaining a constant spinning process, if the lamellas are provided with protrusions on their outer side.

The spinning electrode contains a system of lamellas arranged radial and longitudinally around the rotation axis of the spinning electrode evenly around its perimeter and provided with tips protruding outwards, while in the position when the tips of the spinning electrode are in the plane perpendicular to the plane of the base material, the peaks of these tips are laying on the equipotent line of the highest intensity of electric field between the spinning and collecting electrode.

According to the claim 9 the lamellas are made of a thin electrically conductive material together with the tips and their peaks. This execution is a simple one and does not increase too much the price of the spinning electrode.

At the same time it is advantageous for starting the spinning process if the tip peaks are bow or tip shaped.

According to the claim 12 the lamellas are made of a flat electrically conductive material and in the outward direction are equipped with tips of a cuboid shape finished with formed peaks.

According to the claim 13 these tips are cylindrical and they are finished with formed peaks.

According to the claim 14 the formed peaks are made of a bevelled surface oriented in the rotation direction of the spinning electrode.

According to another execution the formed peaks are made of bevelled surface oriented in the rotation direction of the spinning electrode, while in the bevelled surface there is created a recess serving for measuring of always same quantity of the taken polymeric solution and for exposure of a batch of polymeric solution to action of electric field between the spinning and collecting electrode.

According to the claim 16 the formed peaks are created by a little seat which with advantage contains the upper deflected surface oriented in the direction of lamella length and towards the rotation direction of the spinning electrode oriented front deflected surface and the rear deflected surface and it enables an ideal exposure of the polymeric solution batch being on the little seat to action of electric field which acts evenly to the batch from all sides.

To reach greater widths of produced layer of nanofibres, at least two side by side laying spinning electrodes are arranged on one axis.

To reach a greater thickness of the produced layer of nanofibres, the spinning electrodes are arranged at least two one after another towards the movement direction of the base material.

To reach a great widths of produced layer of nanofibres, the spinning electrodes are arranged at least two side by side on one axis and at least in two rows one after another, while the spinning electrodes of the following row are situated in place of gaps between the spinning electrodes of the previous row.

At the same time the rows of the spinning electrodes are positioned perpendicular to the movement direction of the base material, or

they are positioned askew to the movement direction of the base material.

Description of the drawing

Examples of the device execution as per the invention are schematically shown in the attached drawings, where the Fig. 1 illustrates a cross section of the device with lamellar spinning electrode with lamellas provided with tips with formed peaks, the Fig. 2 shows a longitudinal section of the device with the spinning electrode with filled coating surface, the Fig. 3a and 3b show a view to the lamellar spinning electrode with flat lamellas, the Fig. 4a and 4b a view to the wave lamellar spinning electrode, the Fig. 5a a view to the lamellar spinning electrode with lamellas equipped with cylindrical tips with formed peaks, 5b a view to lamella with tips arranged in a mutual interval, the Fig. 6 a view to lamellar spinning electrode with lamellas provided with tips of a cuboid shape, the Fig. 7a a detail of formed peaks of a flat lamella of the lamellar spinning electrode, the Fig. 7b the peaks of tips of the lamellar spinning electrode with a simple bevelled surface modified into a shape of dimple, the Fig. 7c the peaks of tips of the lamellar spinning electrode with a simple bevelled surface modified into a shape of dimple, the Fig. 7d the peaks of tips of the lamellar spinning electrode with a little seat, the Fig. 8a a serial arrangement of the spinning electrodes, the Fig. 8b a parallel arrangement of the spinning electrodes, the Fig. 8c a serial and a parallel arrangement of spinning electrodes in combination and with shift by a half length of the spinning electrodes and the Fig. 8d an arrangement according to the Fig. 8c with a rotation axis of the spinning electrodes in a different directions towards the shift direction of the base material.

Examples of embodiment

A device for production of nanofibres from the polymeric solution through electrostatic spinning illustrated in the Fig. 1, 3 to 7 contains the spinning electrode 1 created by lamellas 11 arranged radial and longitudinally around the axis 12, which is by a known not illustrated manner pivoted in the body of the equipment. The individual lamellas 11 of the spinning electrode 1 or the whole spinning electrode 1 are in a known not illustrated manner connected with a not illustrated source of a high voltage or grounded. The lamellas 11 are spread along the whole length of the spinning electrode 1 and they are evenly distributed around its perimeter. In the illustrated execution the axis 12 of the spinning electrode is created by a shaft 121, which is by a known not illustrated manner coupled with a drive ensuring its rotation movement.

Under the spinning electrode 1 there is positioned a reservoir 2 with polymeric solution 3. Lamellas 11 in the lower section of the spinning electrode 1 are dipped in the polymeric solution 3. Each lamella contains a lot of tips 111, on the ends of which there are the formed peaks 1111 created, which are the carrying surfaces for the drips 31 of the polymeric solution 3, as illustrated in Fig. 1.

Above the spinning electrode 1 there is arranged the collecting electrode 4 connected in a known not illustrated manner to the source of high voltage of an opposite polarity than the spinning electrode 1 or the grounded one. The axis 12 of the spinning electrode is mounted parallel with the collecting electrode 4, respectively with a plane of the collecting electrode 4. Between the collecting electrode 4 and the spinning electrode 1 , after applying the high voltage to at least of one from them and after grounding of the second electrode, or connecting the second electrode to a high voltage of an opposite polarity, an intensive electric field is created that ensures generation of Taylor cones on the peaks 1111 of the tips 111 of lamellas 11 and drawing of the beam 32 of the polymeric solution 3 from peaks 1111 of the tips 111 towards the collecting electrode 4.

Between the spinning electrode 1 and the collecting electrode 4, usually in the vicinity of the collecting electrode 4, there is performed a guidance for the base material 5, created by the base textile or by another suitable material according to the requirements for usage of the produced textile containing a layer of nanofibres or a textile created by a nanofibre layer. In the illustrated execution the guidance contains two pairs of rollers – the feed rollers 61 and the delivery rollers 62. The base material may be created by an infinite band mounted on a pair of rollers out of which at least one is driven, while the nanofibre layer is picked up from the infinite band by a known manner and is deposited into the package. The movement direction of the base material 5 is usually concurrent with the rotation direction of the spinning electrode 1. To increase the evenness of the layer applied 33 of nanofibres it is nevertheless advantageous to reverse the direction of rotation of the spinning electrode 1 and to rotate the spinning electrode 1 against the sense of movement of the base material 5.

The formed peaks 1111 are created by small surfaces formed for optimalization of the shape of drip 31 of polymeric solution 3 on the formed peak in electric field after carrying out the polymeric solution from the reservoir by the lamella 11. Each such drip 31 represents a batch of polymeric solution 3 brought into the electric field for spinning.

The Fig. 2 shows an alternative of execution of a device for production of nanofibres from water polymeric solution through electrostatic spinning according to the invention. In this case, when compared with the WO 2005/024101 A1, the cylindrical body creating the spinning electrode 1 is formed in a plane running through the axis 12 of rotation of the spinning electrode 1 and perpendicular to the plane of the base material 5 into the shape of equipotent line of electric field between the spinning electrode 1 and the collecting electrode 3 of the highest intensity for the selected potential of electric field. The coating surface of the spinning electrode 1 is filled and is not created by lamellas arranged along the length of the spinning electrode 1, as it is at the above described executions. At the execution of the spinning electrode 1 according to the Fig. 2 it is possible to shape the outer surface e.g. by means of the radial protrusions in the form of collars or tips, protrusions in the shape of spiral or axial protrusions like at the WO 2005/024101 A1.

In other alternative execution which is not illustrated, for production of nanofibres especially of water polymeric solutions, the spinning electrode may be created of system of wheels arranged coaxially side by side on a common shaft, while the coating surface of such system lies in a plane running through an axis of the spinning electrode and perpendicular to the plane of base material created by the equipotent line of electric field between the spinning and collecting electrode of the highest intensity for the selected potential of electric field. At the same time the wheels may be arranged closely side by side or with a certain spacing and they may be provided with protrusions of various shapes on their perimeter.

The execution of the spinning electrode <u>1</u> for spinning of polymers both from non-water and water solutions is illustrated in Fig. 3a in a general view and in Fig. 3b in detail of portion of the electrode. The spinning electrode <u>1</u> contains the shaft <u>12</u>, on which the faces <u>122</u> are attached and in them the flat oblong lamellas <u>11</u> are mounted in radial manner, on which are formed outwards protruding flat tips <u>111</u> finished with formed peaks <u>1111</u>, which are shaped into the form of bow. The tips <u>111</u> of individual lamellas <u>11</u> have a different length, while their coating curve is an equipotent line of electric field made between the spinning electrode <u>1</u> and the collecting electrode <u>4</u> in a plane passing through an axis <u>12</u> of the spinning electrode and perpendicular to the plane of base material <u>5</u>.

Another example execution of the spinning electrode <u>1</u> for spinning of polymers from water as well as non-water solutions is shown in the Fig. 4a in a view against the electrode axis, and the Fig. 4b shows arrangement of lamellas with respect to the shaft in axonometric view. At this execution the lamellas <u>11</u> are created by a corrugated flat electrically conductive material and they are with their ends mounted in the faces <u>122</u> attached to the shaft <u>121</u>, at the same time with respect to the shaft <u>121</u> the lamellas <u>11</u> are mounted tangentially with their corrugation. In the direction outwards from the spinning electrode <u>1</u> a thin surface of lamella serpentine <u>11</u> is directed, which in the radial direction in a plane perpendicular to plane of the base material and passing through a centre of the wavy lamella <u>11</u> is shaped into the form of equipotent line of the highest intensity for the selected potential of electric field created between the spinning electrode <u>1</u> and the collecting electrode <u>4</u>. In the not illustrated example of execution the individual lamellas <u>11</u> are provided with protrusions on their outer side.

The example of execution according to Fig. 5a shows the spinning electrode <u>1</u> for spinning of polymers from water as well as non water polymeric solutions <u>3</u>, which contains on the shaft <u>121</u> attached faces <u>122</u>, between which are in radial manner mounted the lamellas <u>11</u> provided with outwards aiming tips <u>111</u>, which are finished with formed peaks <u>1111</u>. The coating curve of the peaks <u>1111</u> of lamella tips represents an equipotent line of the highest intensity of electric field created between the spinning electrode <u>1</u> and the collecting electrode <u>4</u> in a position, when the tips **111** of the spinning electrode are in a plane perpendicular to the plane of the base material **5**.

In execution according to the Fig. 5a the tips **111** are of a cylindrical shape, they are arranged closely side by side a their formed peaks **1111**, illustrated in a detail view in Fig. 7c contain a bevelled surface **1111a**, in which there is a recess **1111b**, which in an advantageous case is of a ball or cone shape. The formed peak **111** of lamella of the spinning electrode is in other execution created by a bevelled surface **1111a** only as shown in the Fig. 7b, or by a little seat **1111c**, illustrated in Fig. 7d. The little seat contains the upper deflected surface **S1** oriented in the direction of length of lamella **11** and the front deflected surface **S2** oriented with respect to the rotation direction of the spinning electrode forwards and the rear deflected surface **S3** oriented with respect to the rotation direction of the spinning electrode backwards. In the not illustrated execution the front and the rear surfaces of the little seats **1111c** may be created by a flat bevelled surfaces. In another not illustrated execution in the upper deflected surface of the little seat **1111c** there may be created a recess or a dimple.

The Fig. 5b shows an example execution of lamella of the spinning electrode according to Fig. 5a, at which the tips **111** are on the lamella **11** arranged with a certain spacing. The formed peaks **1111** contain the bevelled surface **1111a**, in which the recess **1111b** is provided. The coating curve of the tip peaks **1111** of lamella represents an equipotent line of electric field created between the spinning electrode **1** and the collecting electrode **4**.

The spinning electrode according to Fig. 6 contains the flat lamellas **11** of a certain thickness which are similarly as at the previous execution mounted on a shaft and in the direction outwards they are provided with protrusions of a cuboid shape arranged separately one from another and finished at their ends with formed peaks **1111** that are created by a bevelled surface **1111a**. The formed peaks **1111** of lamellas may be created also by another, especially by that above mentioned manner, i.e. for example by a recess **1111b** or little seats **1111c**.

The spinning electrodes 1 may, for a purpose to reach a greater width possibly a greater evenness and/or greater thickness of the produced nanofibres layer 33 , be arranged in a various manners, as it is shown in Fig. 8a to 8d.

In the execution according to Fig. 8a there are in one axis 12 in a specified spacing one from another positioned at least two spinning electrodes 1, in the illustrated example of execution there are three spinning electrodes 1. The distance between the spinning electrodes 1 has been chosen so that the layer 33 of nanofibres is created on the base material 5 even between the electrodes.

At the execution according to Fig. 8b there are arranged three electrodes 1 in three rows 1210, 1220, 1230 one after another in the direction of movement of the base material 5. This execution has been designed to reach a greater thickness of the layer 33 and it must contain at least two spinning electrodes 1 in two rows one after another.

To reach a greater width of the produced layer 33 of nanofibres and a greater evenness of the layer 33 of nanofibres the spinning electrodes 1 are arranged at least two side by side on one axis 12 and at least in two rows one after another, while the spinning electrodes 1 of the second row 1220 are situated in places of gaps between the spinning electrodes 1 of the first row 1210.

The rows 1210, 1220, 1230 and 1240 of the spinning electrodes 1 are in execution according to Fig. 8c positioned perpendicularly to the direction of movement of the base material 5.

The rows 1210, 1220, 1230 and 1240 of the spinning electrodes 1 are positioned askew to the direction of movement of the base material 5.

The polymeric solution 3 is in a form of defined drips carried out into the electric field pole on the tip peaks 111 of special lamellas 11, which, in arrangement radial and longitudinal along the axis 12 of rotation, rotate on a common axis. The height of tips 111 ensures that the peaks 1111 of these tips are when passing the plane perpendicular to the plane of the base material 5 and running through the axis 12 of rotation of the spinning electrode 1 in the equipotent lines of electric field. Simultaneously a small surface on peaks of the tips 111, being roughly around 1 mm^2, ensures a local increase of electric field in the place of drips, which provides optimum conditions for starting the spinning process. The peaks **1111** of the tips **111** after then may have various finishes , which more or less optimise the shape of the drips. In the most simple arrangement it may be a level surface **1111a** or a recess **1111b**, and in more complex variant e.g. a little seat **1111c**, the usage of which is very advantageous. The little seat **1111c** ensures that the drip will be exposed to electrical field in a symmetric manner and simultaneously the stored polymeric solution **3** will better wash the peaks from remnants of polymeric solution **3**, which has already passed the process.

As mentioned above, to start the process of spinning it is necessary that the polymeric solution **3** (optimally a small portion of its volume) gets into an intensive electrical field. Through experiments it has been proven that the water polymeric solutions **3** differ in principle from the non-water polymeric solutions **3** in the meaning of spinning using the electrostatic forces. The result is not as much surprising, because the water molecule through its small dimension and the strong dipole moment is in an outstanding position towards all other common solvents which have the molecules larger and with lower or nearly no dipole moment. The values of static relative dielectric constant ε_r, when water has 81, acetone 21,4, ethanol 25,1 etc., give also evidence of the totally different character of water. Solvent represents in solutions the main mass (commonly around 80% of wt.) and it defines basically the properties of a polymeric solution. The polymeric solution which is created mostly or totally by molecules non-polar will assume a different attitude towards the external electric field than the polymeric solution containing a quantity of polar molecules. It is known that the dipole similarly to the magnetic needle in magnetic field assumes towards the external electric field a clear attitude, namely so that the vector of dipole is parallel with vector of electric field. The molecules, at which the chaotic movement prevailed before, are enforced to a more consistent internal arrangement within the solution. Hence, the water polymeric solutions are capable of internal layering to polarised layers, which finally causes that there is an intensive electric field as well as the whole surface of the liquid. The polymeric solutions from nearly non-polar or non-polar solvents are practically immune towards the external electric field, and the field does not affect an internal re-arrangement of molecules. On surface of such polymeric solutions the strong electric field is not created, on the contrary the original field is weakened and the rate of weakening is then given by the dimensions of the liquid body (large surface and thickness considerably weaken the intensity of electric field), which after then plays a role of simple insulator. Thus, it is necessary to ensure the field of a high intensity through another way, for the purpose of which the above mentioned structure of the spinning electrode 1 serves. The peaks 1111 of lamella tips in the form of small spots (cca 1 - 4 mm^2) ensure for the drip, which gets stuck on them that it gets into the electric field of a such intensity, which is especially in places of contact of the drip with edge of lamella tip 111 (so called triple point – contact spot of three dielectric different media), and consequently it initiates creation of Taylor cones, drawing of the beam of polymeric solution 3 against the collecting electrode 4. The Taylor cones are a general effect, they are a result of forces to which the polymeric solution is subjected to and their creation occurs once the external force (here the coulomb one) whose vector is perpendicular to the tangential plane to the liquid surface in place of action; it begins to prevail over the forces developed by the inner consistency of liquid molecules and forces of surface tension.

Practically all solutions of polymers in non-water solvents belong to the polymeric solutions with a minimum chance for internal change in environment of electric field. Necessary to say, that the polymeric solution itself, to be able to initiate the spinning process, must meet even further parameters, such as solution viscosity given by the molecular mass of polymer, by its concentration and temperature, further the suitable surface tension given by the type of polymer and presence or non-presence of a surface active substance and a suitable value of electric conductivity of the solution which can be, if necessary, increased by adding the low-molecular electrolyte.

The quantity of the polymeric solution 3 being subject to spinning, thus the total performance may be affected by dimension of the spinning electrode 1. Nevertheless the dimension of the spinning electrode does not affect the performance directly proportional, this even in such a manner that from a certain length of the spinning electrode 3 it starts to be obviously disadvantageous to continue in increasing the length as the performance is then for length unit of the spinning electrode substantially lower with simultaneous increase of unevenness. This is given by the common physical laws accompanying the problems of electric field. The solution arises in a form of various combinations of a larger quantity of „smaller“ spinning electrodes 1, when the individual spinning electrodes 1 are in the parallel or serial arrangement or in combination of both and simultaneously the main axis 12 of the spinning electrodes 1 need not to be perpendicular to the direction of movement of the base material 5 in the continual production system. Next to this, the spinning electrodes may be towards one another in a parallel arrangement shifted by a half of its length, which further contributes to evenness of the applied nanofibre layer 33. The final arrangement is always given by a respective requirement for performance of the machine (width and speed).

Another modification is represented by a rotation of the spinning electrode 1 with respect to the movement of the base material 5 during the continual process. Unevenness in the form of diagonal differences in the applied quantity of the nanofibre layer 33 on the shifting base material 5 , at certain polymeric solutions 3 , may occur due to the fact that the process is being started gradually and separately from each lamella 11. The effective compensation is the speed and rotation direction of the spinning electrode 1. In case of a speed it is optimum if the peripheral speed of the rotating spinning electrode 1 is fifteen times to twenty times greater than the speed of base material 5 movement. Next to this, important is the sense of rotation of the spinning electrode 1 with respect to the direction of movement of the base material 5. The reverse – retrograde rotation of the spinning electrode towards the movement of the base material 5 brings more even results, while the rotation speed need not in such a multiple exceed the speed of movement of the base material 5 as in the case of rotation being concurrent with the movement.

Further modification which is brought by the invention is a usage of various values of voltage on electrodes. It is advantageous to create the potential necessary so that the voltage of opposite polarity is applied to both electrodes (spinning and the collecting one). The electric field is much more better definable and controllable than in a case when the voltage was applied only to one of the electrodes, and as a rule it was the spinning electrode, while to the second electrode (the collecting one) the zero potential was positioned. The zero potential, especially on the collecting electrode, brings a number of disadvantages arising out of the fact that in the vicinity of the spinning area, i.e. the electrodes, another sections of the device are installed, which are also on the zero potential and may in a non-definable manner modify an electric field and to carry away the carried out fibres into the undesirable places. Due to the small currents (roughly hundreds of µA), which are transferred by the charged mass of the polymeric solution, the current circuit may be closed even in spite of the otherwise considerable insulators, like the plastic parts of the device, etc. This is removed by the opposite potential on the collecting electrode, through which the electrode is „made visible" for the material subject to spinning. Much more definable impact of nanofibres to the base material **5** creates the final result of this change.

Example 1

The spinning lamellar electrode according to Fig. 3 rotates in the reservoir of polyamide solution PA 612 (conc. 20 % wt., Mr 2800 g/mol) in an acid. Immersion of the lamella is such that only spots of tips are dipped. The electrode rotates in a retrograde manner towards the movement of the non-conducting spunbond base textile.

Applicability

The method and the device as per the invention are applicable for preparation of layers of nanofibres, especially from polymers soluble in solvents on a non-water basis having the diameter of nanofibres of 100 to 500 nanometers, nevertheless also for spinning of polymers from water solutions. These layers may be used for filtration as the battery separators, to create special composites, for production of protective clothing, in medicine and other areas.

CLAIMS

1. Production method of nanofibres from the polymeric solution (3) through electrostatic spinning in electric field created by a difference of potentials between the collecting electrode (4) and pivoted spinning electrode (1) of an oblong shape touching by a part of its circuit the polymeric solution (3), while by rotation of the spinning electrode (1) the polymeric solution (3), at least by a portion of its surface, is carried out into the electric field in which on the surface of the collecting electrode (4) the nanofibres are created which are carried to the collecting electrode (3) and deposited on the surface of a basic material (5) guided between the spinning electrode (1) and the collecting electrode (3) in vicinity of the collecting electrode (3), **characterised by that the** polymeric solution (3) on surface of the spinning electrode (1) in a place of intersection of surface of the spinning electrode (1) with the plane interlaid by the axis of the spinning electrode (1) and being perpendicular to the plane of the base material (5), along the whole length of the spinning electrode (1) is subject to the electric field of a maximum and equal intensity, through which a high and even spinning effect is achieved along the whole length of the spinning electrode (1).

2. The method as claimed in the claim 1, **characterised by that the** polymeric solution is brought into the electric field in quantities of same batches divided one from another that are moving around the circular tracks in the electric field, while the mutual position of batches does not change and the batches are arranged in groups of batches, situated along the length of the spinning electrode (1) in a plane running through the axis of the spinning electrode (1) and perpendicular to the plane of base material (5) with respect to the collecting electrode (3) on the equipotent line of the highest intensity of electrical field between the spinning electrode (1) and the collecting electrode. (3).

3. The method as claimed in the claim 2, **characterised by that the** direction of bringing out the polymeric solution (3) batches divided one from another is reverse towards the sense of movement of the base material (5).

4. The device for production of nanofibres from polymeric solution through electrostatic spinning in electric field created by a difference of potentials between the collecting electrode and the pivoted spinning electrode of an oblong shape coupled with a drive and touching by at least a portion of its surface the polymeric solution with the objective to carry out the polymeric solution by these portions of surface into the electric field between the spinning electrode and the collecting electrode, while between the spinning electrode and the collecting electrode the track for passage of the basic material is created, the surface of which from the side of the spinning electrode serves for depositing of the nanofibres created, **characterised by that the** coating surface of portions of surface of the spinning electrode (1) serving for carrying out the polymeric solution (3) into the electric field is, in the plane running through the axis (12) of the spinning electrode and perpendicular to the plane of the base material (5), of a shape created by the equipotent line of electric field between the spinning electrode (1) and collecting electrode (3) being of the highest intensity.

5. The device according to the claim 4, **characterised by that the** coating surface is filled.

6. The device according to the claim 4, **characterised by that the** spinning electrode (1) contains a system of corrugated lamellas (11) made of a flat electrically conductive material, which are towards the rotation axis mounted tangentially with their corrugation, at the same time in a plane perpendicular to the plane of the base material (5) and running through the rotation axis of the spinning electrode and in the centre of the corrugated lamella (11) they have a shape of equipotent line of the highest intensity of electric field between the spinning electrode (1) and the collecting electrode (3).

7. The device according to the claim 6, **characterised by that the** lamellas (11) are provided with protrusions on the outer side.

8. The device according to the claim 4, **characterised by that the** spinning electrode (1) contains a system of lamellas (11) arranged radial and longitudinally around the rotation axis (12) of the spinning electrode (1) evenly around its perimeter and provided with tips (111) protruding outwards, while in the position

when the tips (111) of the spinning electrode are in the plane perpendicular to the plane of the base material (5), the peaks (1111) of these tips are laying on the equipotent line of the highest intensity of electric field between the spinning electrode (1) and the collecting electrode (3).

9. The device according to the claim 8, **characterised by that the** lamellas (11) are made of a thin electrically conductive material together with the tips (111) and their peaks.

10. The device according to the claim 9, **characterised by that the** tip peaks (111) are bow shaped.

11. The device according to the claim 9, **characterised by that the** tip peaks (111) are tip shaped.

12. The device according to the claim 8, **characterised by that the** lamellas (11) are made of a flat electrically conductive material and in the outward direction are equipped with tips (111) of a cuboid shape finished with formed peaks. (1111).

13. The device according to the claim 8, **characterised by that the** tips (111) are cylindrical and they are finished with formed peaks (1111).

14. The device according to any of the claims 8, 12 or 13, **characterised by that the** formed peaks (1111) are made of a bevelled surface (1111a) oriented in the rotation direction of the spinning electrode (1).

15. The device according to any of the claims 8, 12 or 13, **characterised by that the** formed peaks (1111) are made of bevelled surface (1111a) oriented in the rotation direction of the spinning electrode (1), while in the bevelled surface there is created a recess (1111b).

16. The device according to any of the claims 8, 12 or 13, **characterised by that the** formed peaks (1111) are created by a little seat (1111c).

17. The device according to the claim 15, **characterised by that the** little seat (1111c) contains the upper deflected surface (S1) oriented in the direction of lamella length (11) and towards the rotation direction of the spinning electrode (1) oriented front deflected surface (S2) and the rear deflected surface (S3).

18. The device according to any of the claims 4 to 17, **characterised by that the** spinning electrodes (1) are arranged at least two side by side on one axis (12).

19. The device according to any of the claims 4 to 17, **characterised by that the** spinning electrodes (1) are arranged at least two one after another towards the movement direction of the base material (5).

20. The device according to any of the claims 4 to 17, **characterised by that the** spinning electrodes (1) are arranged at least two side by side on one axis (12) and at least in two rows one after another, while the spinning electrodes (1) of the following row are situated in place of gaps between the spinning electrodes (1) of the previous row.

21. The device as claimed in the claim 20, **characterised by that the** rows of the spinning electrodes (1) are positioned perpendicular to the movement direction of the base material (5).

they (5).

22. The device as claimed in the claim 20, **characterised by that the** rows of the spinning electrodes (1) are positioned askew to the movement direction of the base material (5).

AMENDED CLAIMS
received by the International Bureau on 16 November 2006 (16.11.2006); claim 4 has been amended, claims 18-22 were cancelled + STATEMENT

4. The device for production of nanofibres from polymeric solution (3) through electrostatic spinning in electric field created by a difference of potentials between the collecting electrode (4) and the pivoted spinning electrode (1) of an oblong shape coupled with a drive and touching by at least a portion of its surface the polymeric solution with the objective to carry out the polymeric solution (3) by these portions of surface into the electric field between the spinning electrode (1) and the collecting electrode (4), while between the spinning electrode (1) and the collecting electrode (4) the track for passage of the basic material (5) is created, the surface of which from the side of the spinning electrode (1) serves for depositing of the nanofibres created, **characterised by that the** the portions of surface of the spinning electrode (1) serving for carrying out the polymeric solution (3) into the electric field have an coating surface which is, in the plane running through the axis (12) of the spinning electrode and perpendicular to the plane of the base material (5), of a shape created by the equipotent line being of the highest intensity of electric field between the spinning electrode (1) and collecting electrode (4).

5. The device according to the claim 4, **characterised by that the** coating surface is filled.

6. The device according to the claim 4, **characterised by that the** spinning electrode (1) contains a system of corrugated lamellas (11) made of a flat electrically conductive material, which are towards the rotation axis mounted tangentially with their corrugation, at the same time in a plane perpendicular to the plane of the base material (5) and running through the rotation axis of the spinning electrode and in the centre of the corrugated lamella (11) they have a shape of equipotent line of the highest intensity of electric field between the spinning electrode (1) and the collecting electrode (3).

7. The device according to the claim 6, **characterised by that the** lamellas (11) are provided with protrusions on the outer side.

8. The device according to the claim 4, **characterised by that the** spinning electrode (1) contains a system of lamellas (11) arranged radial and longitudinally around the rotation axis (12) of the spinning electrode (1) evenly around its perimeter and provided with tips (111) protruding outwards, while in the position

To the international Search Report of the international application No. PCT/CZ2006/000037 dated 18.9.2006 we are presenting the following statement:

The features of the claim 1 are not described in any of the documents D1 – D4. At all these solutions the polymeric solution on surface of the spinning electrode in a place of intersection of surface of the spinning electrode with the plane interlaid by the axis of the spinning electrode and being perpendicular to the plane of the base material along the whole length of the spinning electrode is not subject to the electric field of a maximum and equal intensity, because intensity of electric field at all these solutions on perimeters of the spinning electrode is higher. Due to this the highest spinning effect is on perimeter of the spinning electrode and it decreases in the direction towards the middle of its length. Due to this the layer of nanofibres applied on the base material is thicker on the perimeter than in the middle, which decreases the possibilities of its industrial usage.

From the features of the claim 2 in D1 – D4 there is not described the feature that the batches are arranged in groups of batches situated along the length of the spinning electrode in the plane passing the axis of the spinning electrode and being perpendicular to the plane of the base material with respect to the collecting electrode on the equipotent line of the highest intensity of electric field between the spinning electrode and the collecting electrode. Combination of the features of the claim 2 is so new with respect to D1 – D4.

The direction of movement of the base material against the rotation sence of the spinning electrode is described in D1 and illustrated in the Fig. 1, nevertheless we are convinced that this claim is new in combination with foregoing claims.

In the same way in D1 – D4 there are not described the features of the claim 4, because at no of the solutions mentioned here the coating surface with a portion of the surface of the spinning electrode serving for carrying out of polymeric solution into electric field in the plane passing the axis of the spinning electrode and being perpendicular to the plane of the base material, does not have the shape formed of equipotent line of the highest intensity of electric field between the spinning electrode and the collecting electrode. At the solution according to D1, D3 and D4 the coating surface with a portion of the surface of the spinning electrode serving for carrying out of polymeric solution into electric field in the plane passing the axis of the spinning electrode and being perpendicular to the plane of the base material, has the shape of a straight line and at D2 it is a point. In no case it is not the equipotent line of the highest intensity of electric field.

Also the claim 5 is new in comparison with D1 – D4 in combination with the claim 4. In D1 there is illustrated and described the spinning electrode created by the cylinder with a full coating surface, nevertheless this coating surface is not formed of the respective equipotent line.

For the claims 18 – 22 we ask to be omitted.
We have amended Claim No: 4

Dobroslav Musil
Patent Attorney

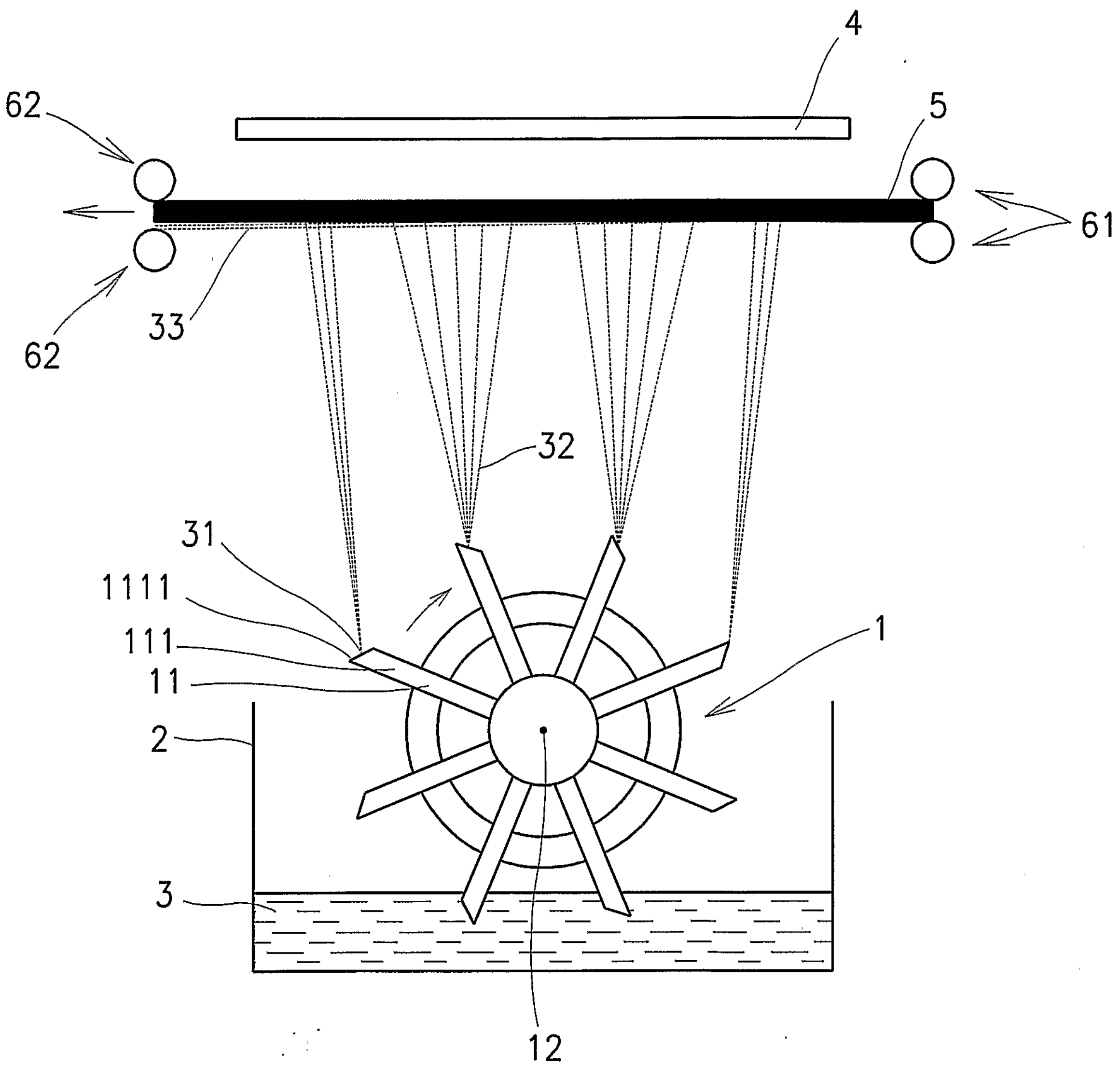


Fig. 1

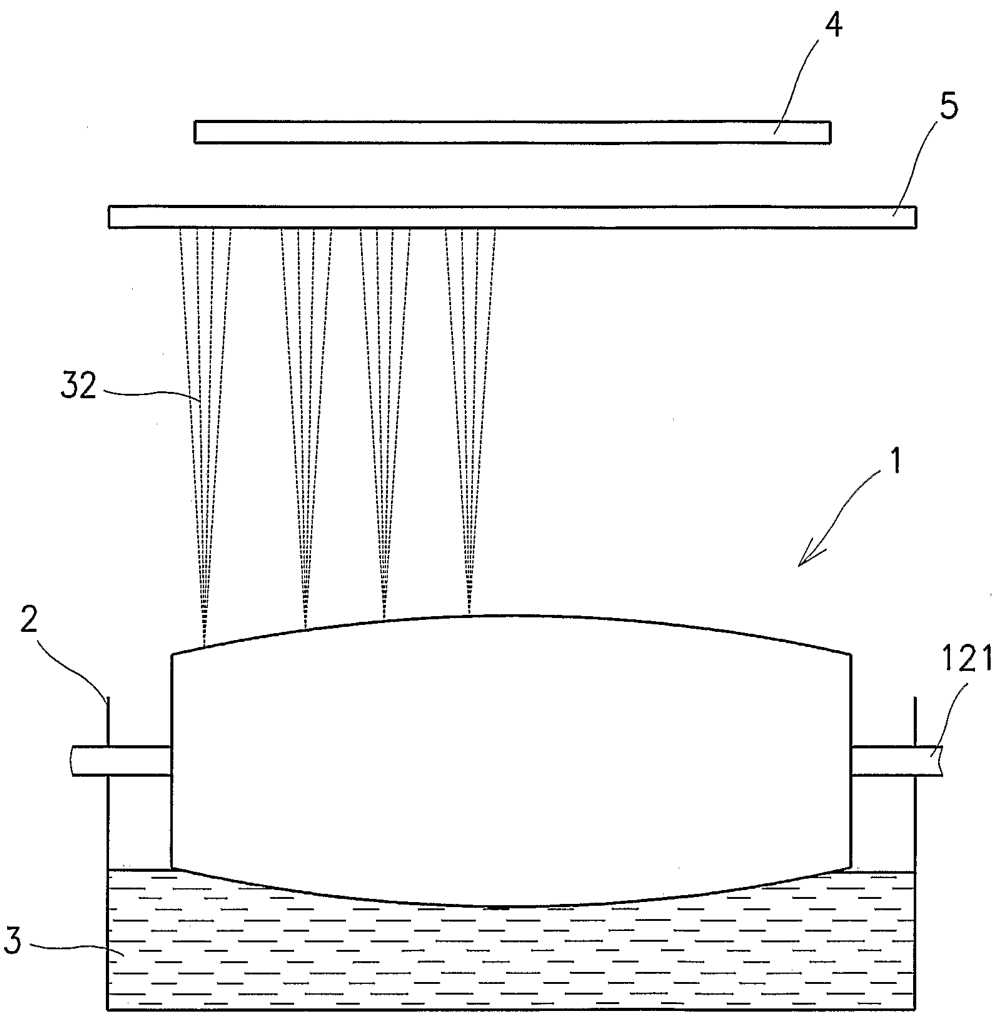


Fig. 2

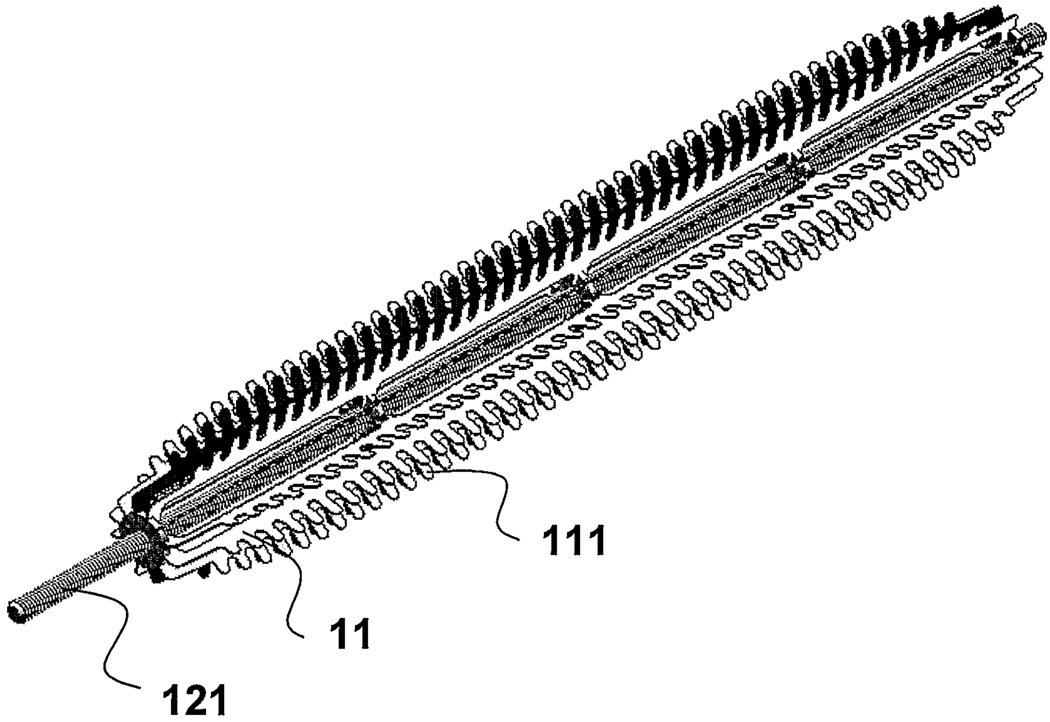


Fig. 3a

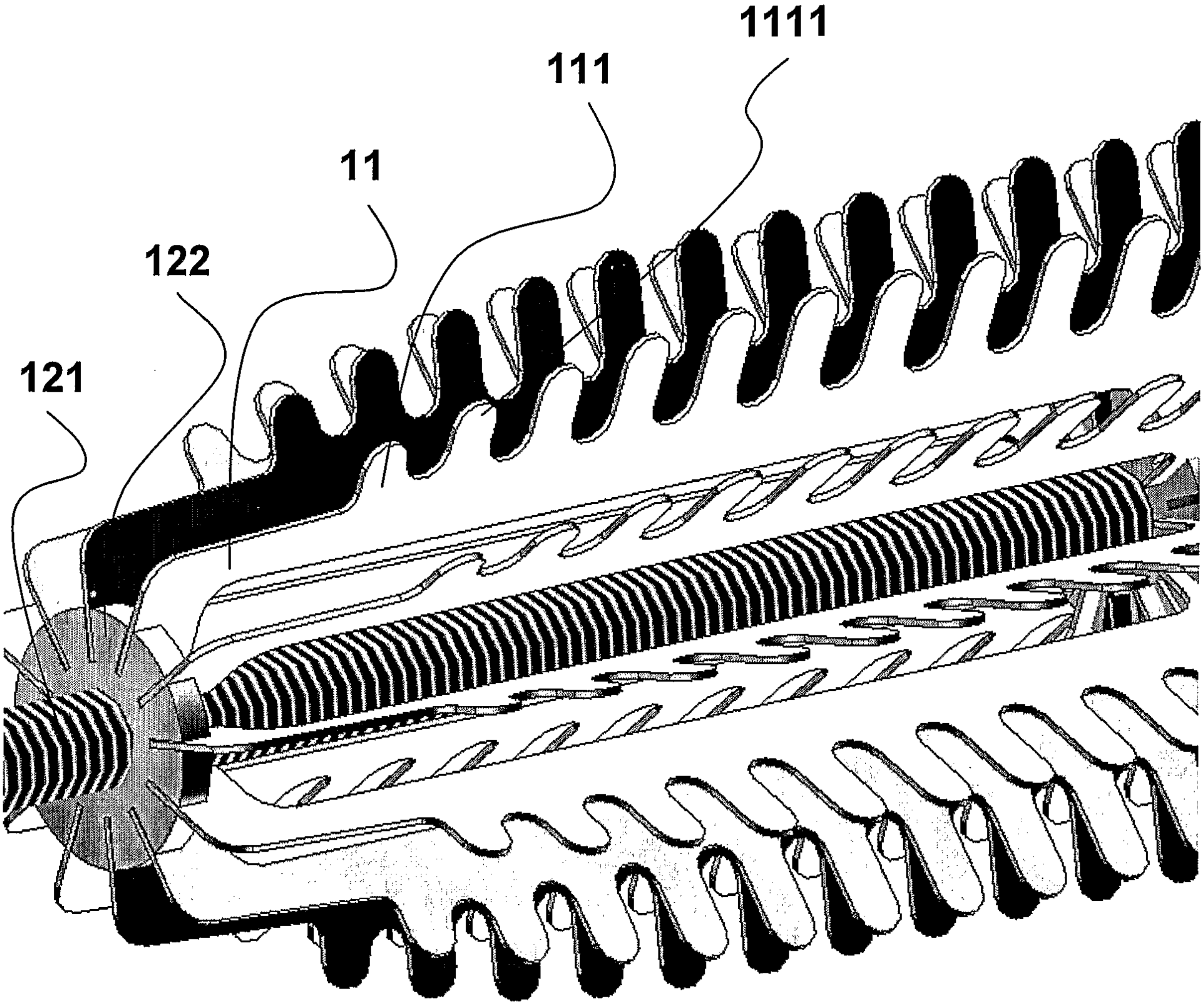


Fig. 3b

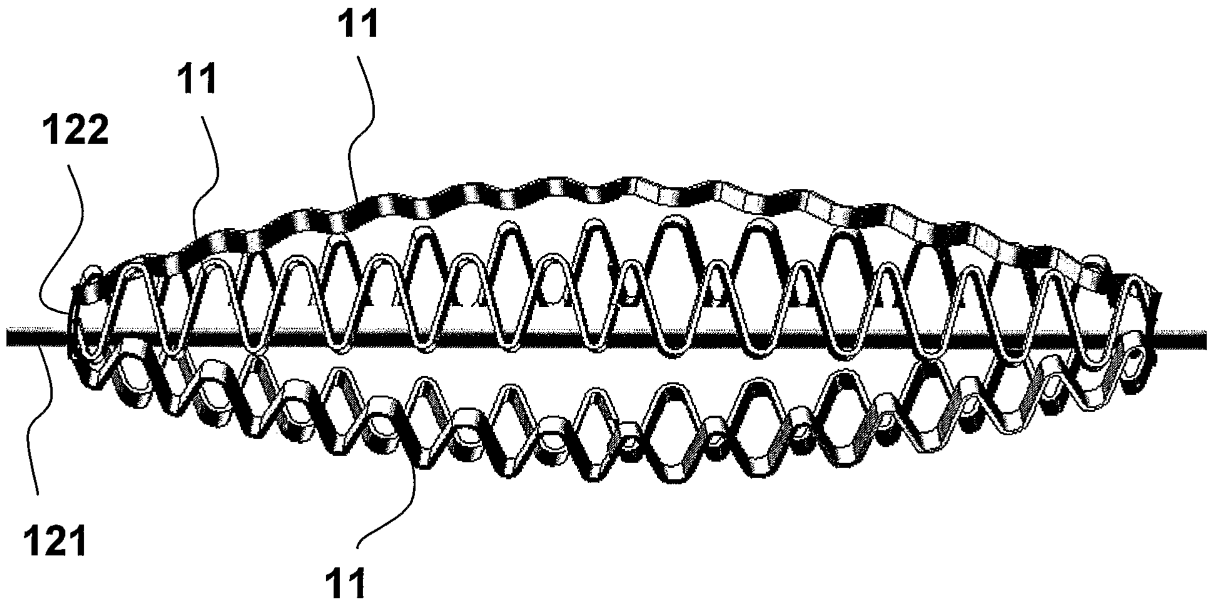


Fig. 4a

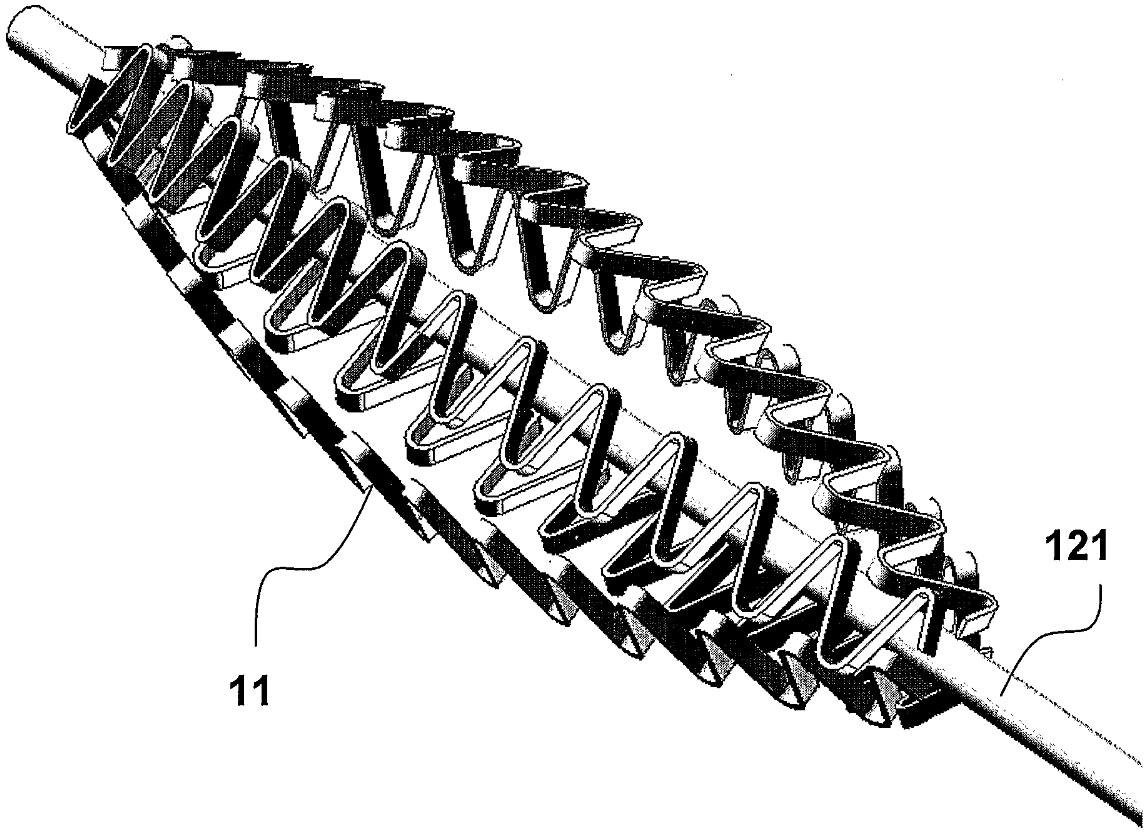


Fig. 4b

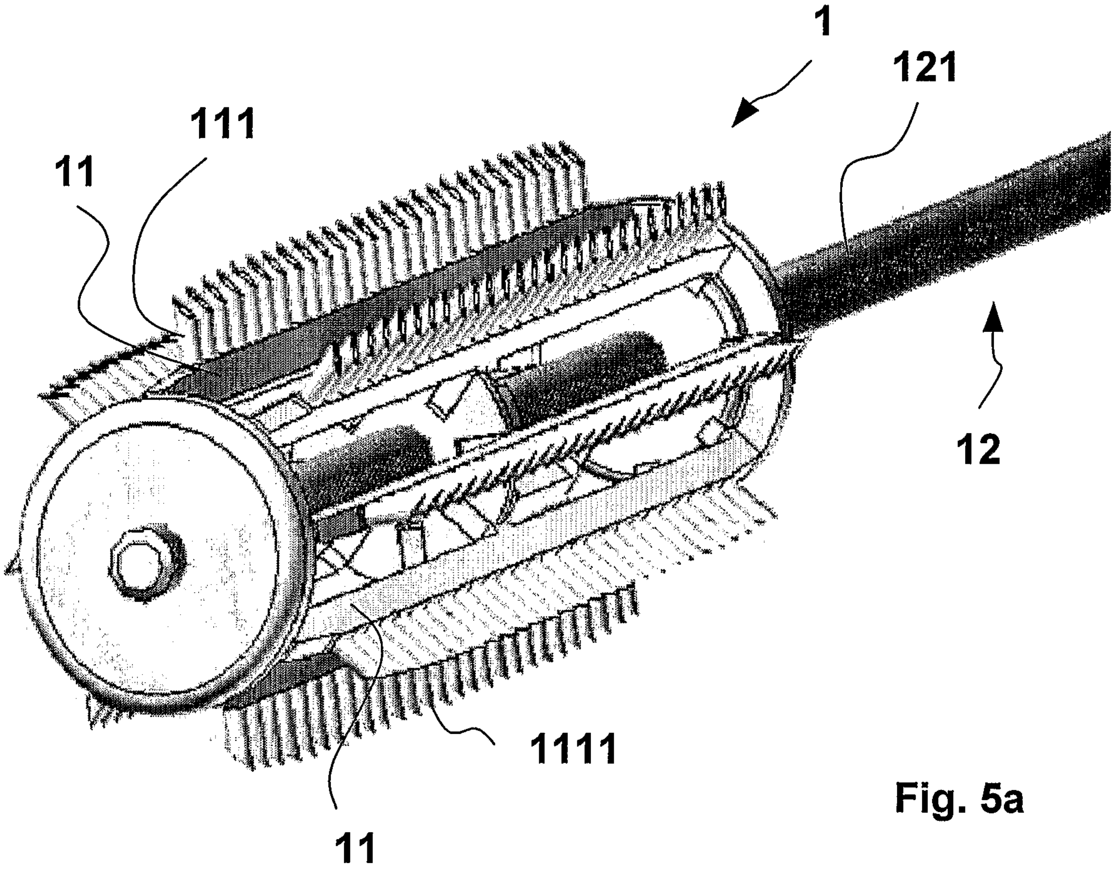


Fig. 5a

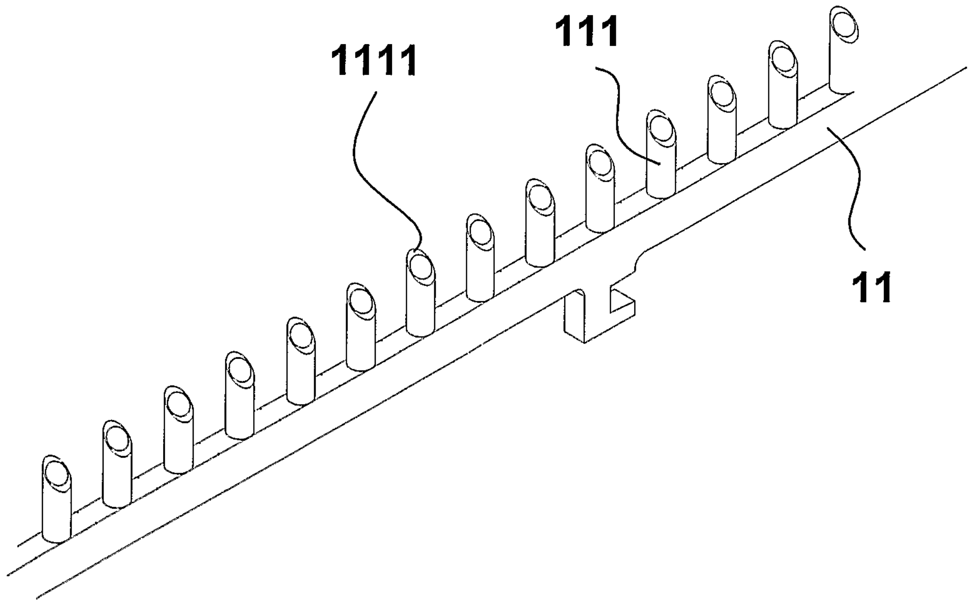


Fig. 5b

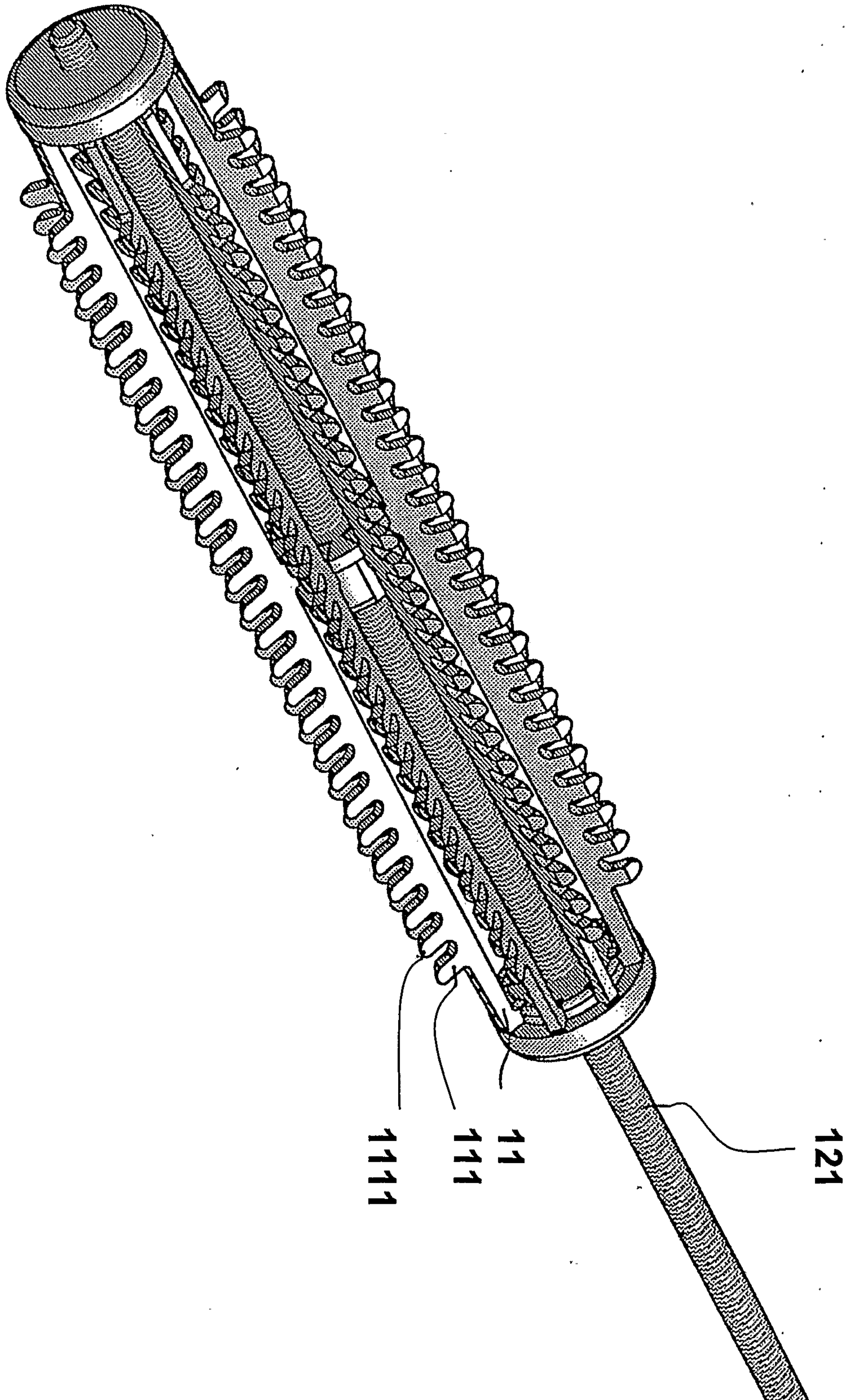


Fig. 6

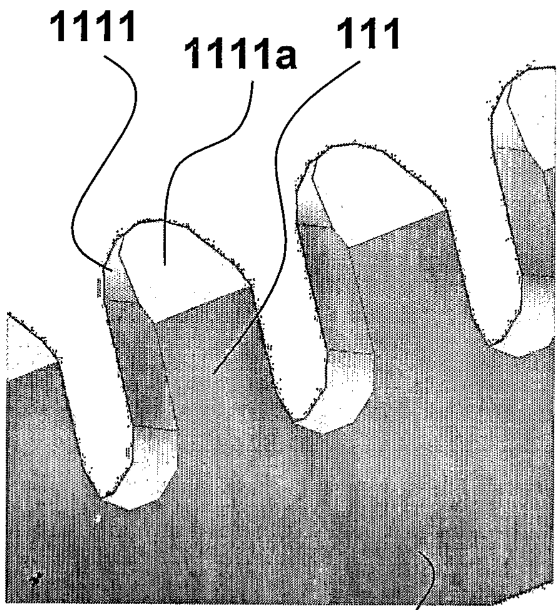


Fig. 7a

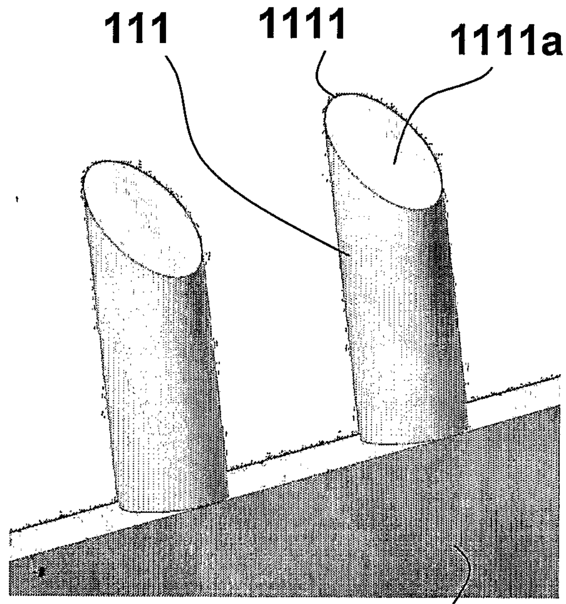


Fig. 7b

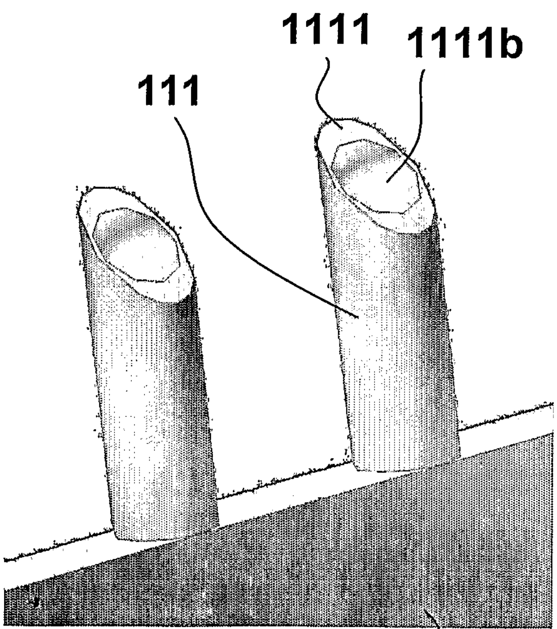


Fig. 7c

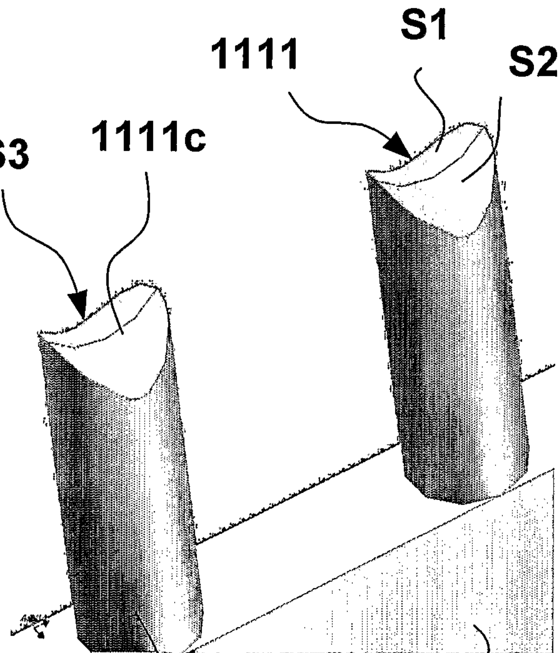


Fig. 7d

Fig. 8a

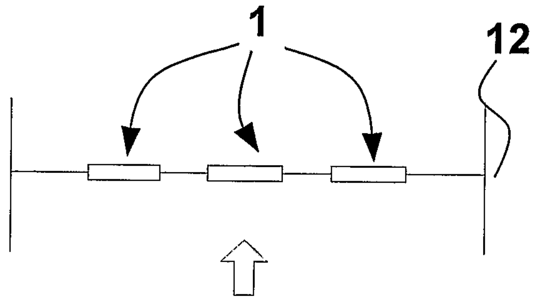
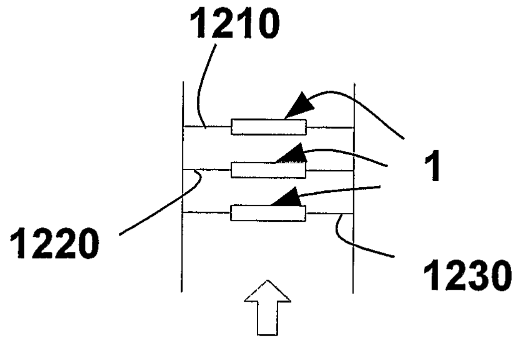


Fig. 8b



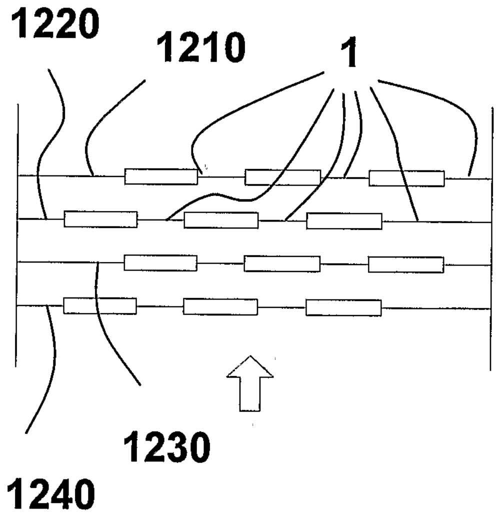


Fig. 8c

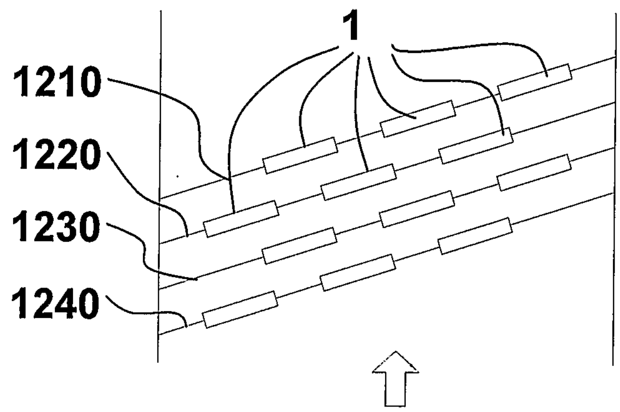


Fig. 8d

INTERNATIONAL SEARCH REPORT

International application No
PCT/CZ2006/000037

A. CLASSIFICATION OF SUBJECT MATTER
INV. D01D5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	GB 1 346 231 A (BAYER AG) 6 February 1974 (1974-02-06) page 1, line 60 - page 3, line 30; figures 1,2	1,4
X	WO 03/016601 A (HELSA-WERKE HELMUT SANDLER GMBH & CO. KG; CZADO, WOLFGANG) 27 February 2003 (2003-02-27) page 2, line 9 - page 3, line 14; figures 1-5	1,4

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 September 2006	18/09/2006

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Mangin, Sophie

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INTERNATIONAL SEARCH REPORT

International application No
PCT/CZ2006/000037

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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1

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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