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

#### (19) World Intellectual Property Organization

International Bureau





(10) International Publication Number WO 2014/079400 A1

(43) International Publication Date 30 May 2014 (30.05.2014)

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

(21) International Application Number:

PCT/CZ2013/000147

(22) International Filing Date:

11 November 2013 (11.11.2013)

(25) Filing Language:

Czech

(26) Publication Language:

English

(30) Priority Data:

PV 2012-834 23 November 2012 (23.11.2012)

CZ

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- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

#### **Declarations under Rule 4.17:**

of inventorship (Rule 4.17(iv))

#### Published:

— with international search report (Art. 21(3))

# (54) Title: METHOD AND DEVICE FOR PRODUCTION OF NANOFIBERS BY ELECTROSTATIC SPINNING OF POLYMER SOLUTION OR MELT

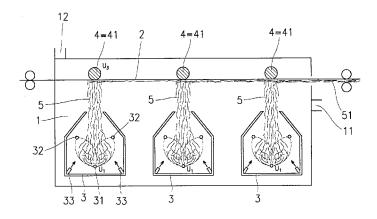


Fig. 1

(57) **Abstract**: Method and device for production of nanofibers by electrostatic spinning of polymer solution or melt The invention relates to a method for production of nanofibers by electrostatic spinning of a polymer solution or a polymer melt in an electric field of high intensity created by a potential difference between a spinning electrode (31) and a counter electrode (32), which are composed of mutually parallel oblong bodies, whereby spinning is performed from the surface of the polymer solution or the polymer melt on the spinning electrode (31) and the created nanofibers (5) are by to the action of the electric field carried towards the counter electrode (32). Spinning is carried out from the surface of the polymer solution or polymer melt on the spinning electrode (31) against at least one pair of counter electrodes (32), which are in relation to the spinning electrode (31) arranged in the same distance and the angle between the planes interlaid by the spinning electrode (31) and both counter electrodes (32) of the corresponding pair of counter electrodes (32) is in the range of 40° to 180°, whereby streams of nanofibers (5) which are directed to each of the counter electrode (32) are before falling on the corresponding counter electrode (32) deflected by the action of the additional force acting in a direction across the stream of nanofibers (5) and are carried by this additional force towards a collecting place (4) of nanofibers (5). The invention also relates to a device for production of nanofibers.





Method and device for production of nanofibers by electrostatic spinning of polymer solution or melt

### **Technical field**

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The invention relates to a method for production of nanofibers using electrostatic spinning of a polymer solution or a polymer melt in an electric field created by a potential difference between a spinning electrode and a counter electrode, which are formed by mutually parallel oblong bodies, whereby spinning is performed from the surface of the solution or polymer melt on the spinning electrode and the created nanofibers are carried towards the counter electrode by to the action of the electric field.

The invention also relates to a device for production of nanofibers using electrostatic spinning of polymer in an electrostatic field of high intensity induced between a spinning electrode and a counter electrode, which are formed by mutually parallel oblong bodies, on whose surface a layer of a polymer solution or polymer melt is created repeatedly or continuously.

#### **Backgound art**

In known electrostatic spinning devices, the created nanofibers are deposited into a layer of nanofibers on a substrate arranged between the spinning electrode and the collecting electrode, between which an electrostatic field of high intensity is created for spinning. In some cases there is a requirement that the place of depositing nanofibers should be outside the space between these electrodes, which is solved in different ways.

From EP 1673493 there is known a method for production of nanofibers from a polymer solution by electrostatic spinning in an electric field created by a potential difference between a rotating charged electrode and a counter electrode, in which the polymer solution for spinning is supplied to the electric field for spinning by means of the surface of the rotating charged electrode, which is by part of its surface immersed in the polymer solution, whereby the created nanofibers are carried away from the rotating charged electrode

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towards the counter electrode by the action of the electric field and subsequently the nanofibers are deposited on a means for depositing of nanofibers. The counter electrode may be formed by a plate, a rod or a system of parallel rods. Nanofibers are created from the surface of cylindric or quadrangular or multiangular prism charged electrode, wherein the counter electrode is located against the free part of the circumference of the charged electrode and the air between the charged electrode and the counter electrode is sucked off. In one of possible variants of embodiment of invention the nanofibers are by sucking the air off deflected from their direction towards the counter electrode and are led to the means of depositing nanofibers, which is arranged outside the space between the electrodes and is pervious to air.

With respect to the fact that in order to deflect the nanofibers from their course between the spinning electrode and counter electrode the air is sucked off from the entire space of the spinning chamber, this method of depositing nanofibers outside the space between the electrodes is energetically demanding.

JP2005264374 describes a device for production of fibres similar to cotton using electrostatic spinning from a polymer solution, in which the spinning proceeds in a spinning chamber between a spinning nozzle and a counter electrode, which are arranged horizontally, whereby the fiber stream is deflected by an air stream which passes across the spinning chamber, whereas the air is led to the chamber at the top and sucked off at the bottom through a substrate material on which the produced fibers are deposited. This device appears to be as energetically demanding as the method described above.

WO 2010/055693 discloses a method for production of nanofibers in which nanofibers are created by a means of electrostatic spraying, which consists of a spinning nozzle connected to one pole of a high voltage source and a collecting electrode connected to the opposite pole of the high voltage source, whereby an air stream is fed in the direction perpendicular to the mouth of the spinning nozzle and is directed towards the surface of the collecting electrode, the air stream blowing the polymer solution from the mouth of the spinning nozzle to the surface of the collecting electrode and facilitating the

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creation of nanofibers, which are deposited on the surface of the collecting electrode.

The drawback of this method is mainly that the spinning nozzle is subject to clogging and that leads to a short-term service life. Another disadvantage is irregularity of the deposited layer of nanofibers as a result of using a narrow air stream for spraying.

WO 2012/066929 describes a device for producing nanofibers, which is configured so that a spinning nozzle is created for spinning a polymer material between the aperture of a spinning nozzle and a metal sphere arranged opposite, both of them being connected to a high voltage source, and between them an electrostatic field of high intensity is created, thus on the surface of the polymer material outgoing from the spinning nozzle there are creatednanofibers which are carried out by the electrostatic field towards the metal sphere. A high-speed air stream jet nozzle leads to the space between the metal sphere and the spinning nozzle, the air stream from the jet nozzle being directed perpendicularly to the path of the nanofibers between the spinning nozzle and the metal sphere. The air stream scatters the nanofibers towards a collecting device whose collecting surface is grounded and is used for gathering and collecting the nanofibers. A plurality of units formed by spinning nozzle, a metal sphere and a high-speed air stream jet nozzle are situated in a row next to each other.

The disadvantage of this device is low productivity of materialpoint spinning, the difficulty in setting a plurality of spinning units so that nanofibers created by each of them would have the same parameters and characteristics, and especially the fact that it is impossible to achieve homogeneity all over the surface of the resulting layer of nanofibers.

EP 2173930 describes a method of spinning the liquid polymer material in an electrostatic field between at least one spinning electrode and one oppositely arranged collecting electrode, whereby one of the electrodes is connected to one pole of a high voltage source and the second electrode is connected to the opposite pole of the high voltage source or is grounded, at which the liquid polymer material is in the electrostatic field on the active spinning zone of the cord of the spinning means of the spinning electrode.

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During the process of spinning the active spinning zone of the cord has a stable position in relation to the collecting electrode and the fluid materialis carried to the active spinning zone of the cord either by coating onto the active spinning zone of the cord, or by moving the cord in a direction of its length. This method of spinning has been successfuly applied for coating the polymer onto the stationary active zone of the cord, whereby the resulting structure, quality and homogeneity of the produced layer of nanofibers surpass the above-mentioned The spinning process is performed in a spinning methods and devices. chamber, in which several spinning electrodes formed of cords are arranged and against each of them there is one collecting electrode formed of a rod or wire, or the collecting electrode is formed by plate common to all the spinning electrodes. It is necessary to keep the required working atmosphere in the extensive space of spinning chamber, which involves sucking off the air containing solvents and supplying clean air, so that the concentration of the solvents would not exceed a set value. The air sucked from the working chamber must be subsequently cleaned so that the solvents are removed and then it can be released into the surrounding atmosphere or it can be reused. Considering the amount of the air, this method, too, is rather energetically demanding.

There are also other known methods and devices for production of nanofibers using electrostatic spinning from a polymer solution or a polymer melt in an electric field created by a potential difference between a charged electrode and a counter electrode which are composed of oblong bodies which are located across the spinning chamber and are mutually parallel, whereby the spinned polymer is during spinning on the surface of these bodies situated in time of spinning against the collecting electrode or the spinning takes place from the free surface of the polymer outgoing from orifice of a oblong body of forming the spinning electrode. The created nanofibers are carried from the spinning electrode to the collecting electrode, in front of which they are deposited on a substrate material.

The method of spinning according to EP 1673493, EP 2173930, as well as other methods, in which the polymer is during spinning on the surface of a body of oblong shape which forms the spinning electrode, have proved to be

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successful both because of their productivity and because of the repeatedly achievable uniform quality of nanofibers and homogeneity of the layer of nanofibers. On the other hand, productivity, that is the amount of nanofibers produced per unit time, is physically limited and in principle it cannot be increased on the existing electrostatic spinning devices.

The aim of the invention is to propose a method of electrostatic spinning and a device to carry out the method, which would improve the producticity of nanofibers production as well as reduce the demands for production in terms of energy and ecology, while preserving all the advantages of currently the most advanced electrostatic spinning methods and devices.

## **Principle of invention**

The goal of the invention has been reached through a method of production of nanofibers using electrostatic spinning of a polymer solution or a polymer melt, whose principle consists in that spinning is carried out from the surface of the polymer solution or the polymer melt on a spinning electrode against at least a pair of counter electrodes which are arranged in relation to the spinning electrode in the same distance and the angle between the planes interlaid by the spinning electrode and both counter electrodes of the relevant pair of counter electrodes is in the range from 40° to 180°, whereby streams of nanofibers directed towards each of the counter electrodes are before falling on the corresponding counter electrode deflected by the action of the additional force acting in a direction across the stream of nanofibers and are carried by this additional force towards the collecting place of nanofibers.

The pair of counter electrodes ensures that spinning is performed from one spinning electrode in two directions, in the bove described method, and thus it increases productivity compared to the background art. This results in better utilization of the solution or the melt of the polymer. If the spinning electrode has a circular cross section, the spinning process runs even from half of its surface.

In the embodiments in which the surface of the solution or the polymer melt is created on the entire circumference of the spinning electrode it is

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possible to perform spinning from one spinning electrode towards two pairs of counter electrodes. In this manner, the productivity increases even more and a more uniform consumption of the solution or polymer melt is achieved.

So as to reduce demand for energy, it is advantageous if spinning proceeds in an auxiliary spinning chamber, which is arranged in the main spinning chamber, surrounds the spinning electrode and the counter electrodes along their entire length and is open towards the collecting place of nanofibers arranged in the main spinning chamber. Due to limiting the spinning space by means of the auxiliary spinning chamber the space, in which it is necessary to keep high quality working atmosphere for spinning, has become smaller and the demands for the quality of the working atmosphere in the main spinning chamber are therefore not so high.

Furthermore, it is advantageous if the additional force is generated by the action of at least one air stream entering along the entire length of the spinning electrode to the space between the spinning electrode and the corresponding counter electrode of the corresponding pair of counter electrodes and leading across the space between the spinning electrode and the corresponding counter electrode towards the collecting place of nanofibers. After the streams of nanofibers are deflected, both air streams merge into one.

Additional force may be also generated by the action of the electrostatic field between the spinning electrode and the collecting electrode arranged on the collecting place of nanofibers or/and by the action of underpressure on the collecting place of nanofibers. Additional forces ensure reliable transportation of the nanofibers from the space between the spinning electrode and the corresponding counter electrodes to the collecting place of nanofibers and prevent their scattering, especially in the space of the main spinning chamber.

In the collecting place of nanofibers the nanofibers either are deposited into a layer on a substrate material or on a deposition means by which they are transported outside the space of the main spinning chamber, or they are sucked off into a reservoir of nanofibers.

In order to meet requirements for manufacturing variously modificated nanofibers, nanofibers containing various additives and/or nanofibers with

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different properties of the surface, air streams contain at least one modification agent adhering to the surface of nanofibers and/or react with the material of nanofibers, or, as the case may be, with the particles, which are contained in the material of nanofibers and/or on their surface, whereby the modification agent is chosen from a group which includes at least antimicrobial and/or antibacterial agents, for example silver, TiO<sub>2</sub>, oxides, salts, or agents with hydrophilic or hydrophobic effect, for example silicone or chlorine groups.

For the purpose of achieving other properties of nanofibers it is possible to feed an additional gaseous medium to the auxiliary spinning chamber.

The principle of the device according to the invention consists in that assigned to the spinning electrode is at least one pair of counter electrodes, which are in relation to the spinning electrode arranged in the same distance and the angle between the planes interlaid by the spinning electrode and each of the counter electrodes of the corresponding pair lies in the range of 40° - 180°, whereby into the space between the spinning electrode and each of the pair of counter electrodes there are lead air nozzles being distributed parallel with the spinning electrode and the corresponding counter electrode along their entire length and the direction of the mouth of the air nozzles intersects the connecting line of the spinning electrode and the corresponding counter electrode of the corresponding pair of counter electrodes and is directed to the collecting place of nanofibers. The device according to the invention ensures increasing productivity and better utilization of the polymer subjected to spinning while keeping the quality of nanofibers, since spinning is performed from a greater part of the surface of the polymer on the spinning electrode.

In order to reduce demand for energy, the spinning electrode, together with at least one pair of counter electrodes assigned to it, is along its whole length surrounded by an auxiliary spinning chamber which is arranged in the main spinning chamber and is opened towards the collecting place of nanofibers arranged in the main spinning chamber.

Other advantages and features result from the remaining dependent claims on the device.

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#### Description of drawings

Examples of embodiment of the invention are schematically represented in enclosed drawings, where Fig. 1 shows a cross section of the main spinning chamber of the device in an example of embodiment for spinning in an upward direction, Fig. 2 represents a cross section of the auxiliary spinning chamber and the collecting place of nanofibers comprising a collecting electrode for spinning in a downward direction, Fig. 3 shows a cross section of the auxiliary spinning chamber and the collecting places for spinning in an upward and also downward direction comprising corona electrodes, Fig. 4a is a cross section of an example of embodiment of the device with one pair of counter electrodes, in which the angle between the planes interlaid by the spinning electrode and both counter electrodes of the corresponding pair of counter electrodes is 180°, Fig. 4b provides a view of the embodiment according to Fig. 4a from the left-hand side, Fig. 5 represents the arrangement of the auxiliary spinning chamber, to which the sucking and collecting device of nanofibers is assigned.

#### examples of embodiment

In the example of embodiment shown in Fig. 1 the device for production of nanofibers comprises the main spinning chamber  $\underline{1}$ , into which a substrate material  $\underline{2}$  is fed in a known manner, for example a textile or paper, serving for depositing a layer of nanofibers, the substrate material being drawn from the main spinning chamber  $\underline{1}$  in a known manner, whereby it is kept tight in the spinning chamber  $\underline{1}$ . In the example of embodiment shown in Fig. 1 in the main spinning chamber  $\underline{1}$  three spinning units are arranged, each of them comprising an auxiliary spinning chamber  $\underline{3}$  composed of an oblong body, located along the whole width of the main spinning chamber  $\underline{1}$  and of the collectoing place  $\underline{4}$  of nanofibers  $\underline{5}$ , which is in the illustrated embodiment formed by a collecting electrode  $\underline{41}$ , which is formed by an oblong body located along the whole width of the spinning chamber  $\underline{1}$  and is arranged in a direction away from the auxiliary spinning chamber  $\underline{3}$  behind the substrate material  $\underline{2}$ . The auxiliary spinning chamber  $\underline{3}$  is open towards the collecting electrode  $\underline{41}$ .

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In the lower part of the auxiliary spinning chamber 3 is along its entire length arranged a spinning electrode 31 formed by an oblong body and parallel with the collecting electrode 41. Parallel with it and in the same distance from it there are in the upper part of the auxiliary spinning chamber 3 along its entire length arranged two counter electrodes 32, which are also composed of oblong bodies and are arranged outside the connecting line between the spinning electrode 31 and the collecting electrode 41. The angle between the planes interlaid by the spinning electrode 31 and the corresponding counter electrodes 32 is in the range of 40° - 180, preferably in the range of 60°- 180°. The spinning electrode 31 is connected to one pole of a high voltage source and the counter electrodes 32 are connected to the opposite pole of the high voltage source or are grounded, by which means between the spinning electrode 31 and each of the counter electrodes 32 an electrostatic field of high intensity is created, which is indicated in the drawings by dash-dotted lines. Also the collecting electrode 41 is in this embodiment connected to the opposite pole of the high voltage source than the spinning electrode 31, thus an electrostatic field is created between them, although its intensity is lower due to the distance between the electrodes, which is greater than the distance between the spinning electrode 31 and the counter electrodes 32, in spite of the fact that the difference in voltage between the spinning electrode 31 and the collecting electrode 41 is greater than the difference in voltage between the spinning electrode 31 and each of the counter electrodes 32. To the space of the auxiliary spinning chamber 3 there are led air nozzles 33, which are distributed along the whole length of the auxiliary spinning chamber 3 and further lead across the connecting line of the spinning electrode 31 and the corresponding counter electrode 32 to the space between the counter electrodes 32 and the air streams created by them are directed after merging into one to the orifice of the auxiliary spinning chamber 3 and towards the collecting electrode 41.

On the spinning electrode <u>31</u>, using any of the known methods, the surface of the polymer solution or polymer melt is created continuously or repeatedly and from this surface in a direction towards the corresponding counter electrode <u>32</u> the polymer is subjected to spinning. The spinning electrode <u>31</u> can be created by any known method according to the background

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art. Nowadays the most suitable spinning electrode appears to be the cord spinning electrode according to EP 2173930, on which the polymer solution is repeatedly applied by a coating device moving parallel with the cord along its active spinning zone.

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The counter electrodes <u>32</u> can also be created by any known method according to the background art, for example they can be composed of a plate or a rod or a group of rods or a cord or a group of cords, whereby the most suitable type appears to be a rod or cord counter electrode. If cord counter electrodes are used, they may be coupled with means of their winding and/or cleaning for the purpose of possible removing nanofibers <u>5</u>, which were not deflected by the action of the additional force towards the collecting place <u>4</u> of nanofibers <u>5</u>, in this case towards the collecting electrode <u>41</u>.

Also, the collecting electrode <u>41</u> may be composed of at least one of any collecting electrodes known from the background art, whereby nowadays the most suitable type appears to be a rod or cylindric collecting electrode, which is in contact with the substrate material <u>2</u>, or a corona collecting electrode arranged out of contact with the substrate material <u>2</u>.

The substrate material <u>2</u> may be in all embodiments replaced with a known conveyor belt arranged on the collecting place <u>4</u> of nanofibers <u>5</u> and forming at the same time a collecting electrode <u>41</u>, as is shown in Fig. 5. Assigned to the conveyor is a collecting vessel <u>6</u> of nanofibers <u>5</u> or of a nanofibrous layer <u>51</u> and unillustrated means of taking off the nanofibers <u>5</u> or the nanofibrous layer <u>51</u> from the conveyor.

The air nozzles  $\underline{33}$  are formed for example by flat nozzles which are distributed along the whole length of the auxiliary spinning chamber  $\underline{3}$ , or they may be formed by a system of nozzles arranged along the whole length of the auxiliary spinning chamber  $\underline{3}$  or in another suitable manner that enables to create along the whole length of the auxiliary spinning chamber  $\underline{3}$  a suitable air stream which is in principle flat and which is directed across the connecting line of the spinning electrode  $\underline{31}$  and the corresponding counter electrode  $\underline{32}$  to the space between the counter electrodes  $\underline{32}$ .

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During spinning the surface of the solution or polymer melt is created on the spinning electrode  $\underline{31}$  continuously or repeatedly. The spinning electrode  $\underline{31}$  is fed by the voltage  $\underline{U_1}$  and the counter electrode  $\underline{32}$  is fed by the voltage  $\underline{U_2}$ . The difference between these voltages, whose polarity is usually opposite, or one of the electrodes is grounded, creates between the spinning electrode  $\underline{31}$  and the counter electrodes  $\underline{32}$  an electrostatic field of high intensity, by whose action from the surface of the solution or polymer melt nanofibers  $\underline{5}$  begin to be created on the spinning electrode  $\underline{31}$ . The nanofibres  $\underline{5}$  are by the action of the electrostatic field carried towards the corresponding counter electrode  $\underline{32}$ , whereby create in principle regular stream of nanofibers  $\underline{5}$  along the entire length of the spinning electrode  $\underline{31}$  and the corresponding counter electrode  $\underline{32}$ .

On the stream of nanofibers 5 between the spinning electrode 31 and the corresponding counter electrode 32 is acted by an additional force created by an air stream from a corresponding air nozzle 33, by which the nanofibers are 5 before falling on the counter electrode 32 deflected from their original direction to the direction towards the collecting electrode 41, whereupon both air streams merge into one and the nanofibers 5 are in front of the collecting electrode 41 deposited on the substrate material 2 or a means of depositing. The movement of the nanofibers 5 towards the collecting electrode 41 is facilitated by an auxiliary electrostatic field created between the collecting electrode 41 and the spinning electrode  $\underline{31}$  after the voltage  $\underline{U}_3$  is fed to the collecting electrode  $\underline{41}$ . However, due to the great distance between the collecting electrode 41 and the spinning electrode 31 the auxiliary electrostatic field has a lower intensity than the electrostatic fields created between the spinning electrode 31 and the counter electrodes 32, and so the auxiliary electrostatic field does not interfere with the spinning process of creating nanofibers on the surface of the polymer solution or melt on the spinning electrode 31, but it facilitates the drifting of the nanofibers 5 in a direction towards the collecting electrode 41 after being deflected by an air stream and thus increases the additional force created by this air stream.

It is assumed that the intensity of the auxiliary electrostatic field between the spinning electrode <u>31</u> and the collecting electrode <u>41</u> can be set in such a manner that in the portion in front of the falling of streams of nanofibers <u>5</u> on the

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counter electrode <u>32</u> the auxiliary electrostatic field is able to act upon the nanofibers <u>5</u> by an additional force towards the collecting electrode <u>41</u> and deflect at least some of the nanofibers <u>5</u> towards the collecting electrode <u>41</u>. However, for the stability of the process it appears to be more simple and/or more suitable to employ the auxiliary electrostatic field so as to support the additional force created by the air stream, as described above.

with respect to the fact that spinning takes place in the auxiliary spinning chamber 3, in which both the spinning electrode 31, and the counter electrodes 32 are arranged, the requirements for keeping the desirable working atmosphere for spinning are limited to the auxiliary spinning chamber 3, whereas in the space of the main spinning chamber 1 the requirements for the working atmosphere are not so strict, since the nanofibers 5 are only transported through this space by an air stream from the auxiliary spinning chamber 3 and deposited on the substrate material 2. Although the air carrying the nanofibers 5 from the auxiliary spinning chamber 3 contains solvents in amounts approaching the maximum possible value, but the air is scattered within a greater space of the main spinning chamber 1, by which means the concentration of the solvents in the air decreases and the air in the main spinning chamber 1 can be replaced more slowly and in lower amounts, which decreases energetic demands for this replacement and the whole process of spinning. At the same time, the air flows through the main spinning chamber 1 in a known manner through the inlet orifice 11 from the side of the outlet of the substrate material 2 with the deposited layer 51 of nanofibers towards the side of the main spinning chamber 1 with the inlet of the substrate material 2, whereby it can be taken out both from the space under the substrate material 2 and from the space above the substrate material 2, for example through the outlet orifice 12. The inlet orifice 11 and the outlet orifice 12 are formed for example by an aperture along the whole width of the main spinning chamber 1 or by a system of orifices along the width of the main spinning chamber 1. The air that is removed is cleaned in a known way and subsequently either released to the surrounding atmosphere, or taken back to the machine.

To the air fed to the auxiliary spinning chamber  $\underline{3}$  it is possible to add a suitable modification agent adhering to the surface of nanofibers  $\underline{5}$  or reacting

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with the material of nanofibers  $\underline{5}$  or with the particles which are contained in the material of nanofibers  $\underline{5}$ . Modification agents may be agents from the group of antimicrobial and/or antibacterial agents, for example silver,  $TiO_2$ , oxides, salts, or agents with a hydrophilic or hydrophobic effect, for example silicone or chlorine groups, by which means on the surface of nanofibers  $\underline{5}$  a hydrophilic or hydrophobic layer is created, and so the created layer of nanofibers will have hydrophilic or hydrophobic effects. At the same time it is possible to add from each air nozzle a different modification agent in the auxiliary spinning chamber  $\underline{3}$  and to carry out this in all the auxiliary spinning chambers  $\underline{3}$  in the same manner, or to apply a different modification agent in each auxiliary spinning chamber  $\underline{3}$  according to the requirements for the resulting properties of the nanofibrous material. Modification agents can be supplied in gaseous, liquid or solid form, whereby they are scattered to the corresponding air stream in a suitable known manner.

The auxiliary spinning chamber  $\underline{3}$  may be provided with auxiliary nozzles  $\underline{34}$  of a any supplementary gaseous medium into the working atmosphere of the auxiliary spinning chamber  $\underline{3}$ , as is shown in Fig. 5, whereby the supplementary gaseous medium may be additional air, either clear air or air containing modification agents, or  $CO_2$  or another gas that would be required or suitable from the technological point of view, for example inert gas, whereby the temperature of the supplied medium, too, may be adapted. For example, when feeding compressed gas into the auxiliary spinning chamber  $\underline{3}$ , the working atmosphere will be cooled during expanding of the gas, which results in changes in the crystalline structure of nanofibers  $\underline{5}$ .

In the above-described embodiment of a spinning unit illustrated in Fig.1 the auxiliary spinning chamber  $\underline{3}$  is open in an upward direction, the collecting electrode  $\underline{41}$  is arranged above the orifice of the auxiliary spinning chamber  $\underline{3}$  and above the spinning electrode  $\underline{31}$  and the process of spinning proceeds in an upward direction.

Fig. 2 shows an example of embodiment of a spinning unit, in which the auxiliary spinning chamber  $\underline{3}$  is open in a downward direction, the spinning electrode  $\underline{31}$  is arranged in the upper part of the auxiliary spinning chamber  $\underline{3}$  under its upper bottom, the collecting electrode  $\underline{41}$  is arranged in the lower part

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opposite the orifice of the auxiliary spinning chamber 3 and spinning proceeds in the opposite direction than in the embodiment according to Fig. 1.

The example of embodiment according to Fig. 3 represents integration of the embodiments according to Fig. 1 and 2. The auxiliary spinning chamber 3 is open in an upward direction as well as in a downward direction, both orifices being arranged opposite each other. Arranged in the middle of the auxiliary spinning chamber 3 is a spinning electrode 31 formed in the illustrated embodiment by a cord, which is provided with a known device for applying liquid polymer on its entire circumference. Around the spinning electrode 31 four counter electrodes 32 are arranged in a cross, between each of them and the opposite surface of the polymer on the spinning electrode 31 an electrostatic field of high intensity is created and the process of spinning starts. The nanofibers 5 being produced are carried towards the corresponding counter electrode 32 and before falling on it they are deflected by air streams which are emitted from air nozzles 33 arranged on the wall of the auxiliary spinning chamber 3 along its entire length. In the upper part of the auxiliary spinning chamber  $\underline{\mathbf{3}}$  nanofibers are deflected towards the upper orifice of the auxiliary spinning chamber 3, through which they pass and are deposited on the substrate material  $\underline{2}$ . The collecting place  $\underline{4}$  of nanofibers  $\underline{5}$  is in this embodiment composed of a corona electrode 42, which creates a stream of electrons, which is directed towards the spinning electrode 31 and is deposited on the substrate material 2, which then acts as a collecting electrode. The substrate material 2 is in this embodiment out of contact with the corona electrode 42. The lower part of the device works in the same manner as the above-mentioned upper part.

In the example of embodiment according to Fig. 4a, 4b a pair of counter electrodes <u>32</u> is assigned to the spinning electrode <u>31</u>. The angle between the planes interlaid by the spinning electrode <u>31</u> and both counter electrodes <u>32</u> is 180°. Also in this embodiment, air nozzles <u>33</u> lead askew against each other and the streams of air coming out of them merge into one and carry the nanofibers <u>5</u> towards the collecting place <u>4</u> of nanofibers <u>5</u>. In this embodiment, too, it is advantageous if the spinning electrode <u>31</u>, as well as the pair of counter electrodes <u>32</u>, are surrounded along their entire length by the auxiliary

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spinning chamber  $\underline{3}$ , which is arranged in the main spinning chamber  $\underline{1}$  and is open towards the collecting place  $\underline{4}$  of nanofibers  $\underline{5}$ . The auxiliary spinning chamber is not shown in Fig. 4a, 4b.

In the example of embodiment according to Fig. 5 the collecting place <u>4</u> of nanofibers <u>5</u> is formed by a sucking and collecting device <u>43</u> of nanofibers <u>5</u>, which is coupled with an underpressure source. Further the device si equivalent to the device according to Fig.1.

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It is apparent to persons skilled in the art that all the described embodiments can be turned to both sides by the angle of up to 90°, that means when spinning in a vertical direction – upwards or downwards – becomes spinning in a horizontal direction – to the left or to the right.

Similarly, it is evident that the counter electrodes <u>32</u> may be arranged displaceably in relation to the spinning electrode <u>31</u>, as to the distance from the spinning electrode <u>31</u> and also as to the angle between the planes interlaid by the spinning electrode <u>31</u> and both counter electrodes <u>32</u> of the corresponding pair of counter electrodes <u>32</u>. The direction of the mouth of the air nozzles <u>33</u> is adjustable as well.

Also, it is obvious to persons skilled in the art that the spinning electrode may be composed of a system of known spinning nozzles.

## List of references

	1	main spinning chamber
	11	inlet orifice of air
5	12	outlet orifice of air
	2	substrate material
	3	auxiliary spinning chamber
	31	spinning electrode
	32	counter electrode
10	33	air nozzle
	34	auxiliary nozzle
	4	collecting place of nanofibers
	41	collecting electrode
	42	corona electrode
15	43	sucking and collecting device of nanofibers
	5	nanofibers
	6	collecting vessel
	$U_1$	voltage on spinning electrode
	$U_2$	voltage on counter electrode
20	$U_3$	voltage on collecting electrode

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#### **PATENT CLAIMS**

- 1. A method for production of nanofibers by electrostatic spinning from a polymer solution or a polymer melt in an electric field of high intensity created by a potential difference between a spinning electrode (31) and a counter electrode (32), which are formed by mutually parallel oblong bodies, whereby spinning is performed from the surface of the solution or polymer melt on the spinning electrode (31) and the produced nanofibers (5) are by the action of the electric field carried towards the counter electrode (32), characterized in that spinning is carried out from the surface of the solution or the polymer melt on the spinning electrode (31) against a pair of counter electrodes (32), which are arranged in relation to the spinning electrode (31) in the same distance and the angle between the planes interlaid by the spinning electrode (31) and both counter electrodes (32) of the corresponding pair of counter electrodes (32) is in the range from 40° to 180°, whereby the streams of nanofibers (5) which are directed to each of the pair of the counter electrodes (32) are deflected before falling on the corresponding counter electrode (32) by the action of an additional force acting in a direction across the stream of nanofibers (5) and due to this additional force the nanofibers are carried towards the collector (4) of nanofibers (5).
- 2. A method according to Claim 1, **characterized in that** spinning takes place against two pairs of counter electrodes (32).
- 3. A method according to Claim 1 or 2, **characterized in that** spinning is carried out in an auxiliary spinning chamber (3), which is placed in the main spinning chamber (1), surrounds the spinning electrode (31) and the counter electrodes (32) along their entire length and is opened towards the collecting place (4) of nanofibers (5) arranged in the main spinning chamber (1).
- 4. A method according to Claims 1 to 3, **characterized in that** an additional force is generated by the action of air streams which enter along the whole length of the spinning electrode (31) to the space between the spinning electrode (31) and the corresponding counter electrode (32) of the

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corresponding pair of counter electrodes (32) and which are directed across the space between the spinning electrode (31) and the corresponding counter electrode (32) towards the collecting place (4) of nanofibers (5).

- 5. A method according to Claim 4, **characterized in that** the additional force is generated by the action of electrostatic field between the spinning electrode (31) and the collecting electrode (41) arranged on the collecting place (4) of nanofibers (5).
- 6. A method according to Claim 4 or 5, **characterized in that** the additional force is generated by the action of underpressure in the collecting place (4) of nanofibers (5).
- 7. A method according to any of the preceding claims, **characterized in that** nanofibers (5) are deposited on a substrate material (2) or a depositing means arranged in front of the collecting place (4) of nanofibers (5), which is composed of a collecting electrode (41) or a corona electrode (42) connected to a high voltage of opposite polarity than the spinning electrode (31).
- 8. A method according to any of Claims 1 to 6, **characterized in that** the nanofibers (5) are in the collecting place (4) sucked off by a collecting device (43) of nanofibers (5).
- 9. A method according to Claim 4 and any of the following, characterized in that the air streams contain at least one modification agent adhering to the surface of the nanofibers (5) and/or reacting with the nanofibrous material (5), or with the particles that are contained in the nanofibrous material (5) and/or on its surface, whereby the modification agent is selected from a group including at least antimicrobial and/or antibacterial agents, preferably silver, TiO<sub>2</sub>, oxides, salts, or agents with a hydrophilic or hydrophobic effect, such as silicone or chlorine groups.
  - 10. A method according to Claim 3 and any of the following, characterized in that into the auxiliary spinning chamber (3) an additional gaseous medium is fed.

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11. A device for production of nanofibers by electrostatic spinning of a polymer solution or a polymer melt in an electrostatic field of high intensity created between a spinning electrode (31) a counter electrode (32), which are composed of parallel oblong bodies, on whose surface a layer of the solution or melt is created repeatedly or continuously characterized in that assigned to the spinning electrode (31) is at least one pair of counter electrodes (32), which are arranged in relation to the spinning electrode (31) in the same distance and the angle between the planes interlaid by the spinning electrode (31) and each of the counter electrodes (32) of the corresponding pair of counter electrodes (32) is in the range from 40° to 180°, wherein into the space between the spinning electrode (31) and each of the pair of the counter electrodes (32) there lead air nozzles (33), being distributed parallel with the spinning electrode (31) and the corresponding counter electrode (32) along their whole length and the direction of the mouth of the air nozzles (33) intersects the connecting line of the spinning electrode (31) and the corresponding counter electrode (32) of the corresponding pair of counter electrodes (32) and directs to the collecting place (4) of nanofibers (5).

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- 12. A device according to Claim 11, **characterized in that** two pairs of counter electrodes are assigned (32) to the spinning electrode (31).
- 13. A device according to Claim 11 or 12, **characterized in that** the spinning electrode (31) with at least one pair of counter electrodes (32) assigned to it are along their whole length surrounded by the auxiliary spinning chamber (3), which is arranged in the main spinning chamber (1) opened towards the collecting place (4) of nanofibers (5) located in the main spinning chamber (1).
  - 14. A device according to Claims 11 to 13, **characterized in that** the counter electrodes (32) are arranged displaceably in relation to the spinning electrode (31).
- 15. A device according to any of Claims 11 to 14, **characterized in that** 30 the air nozzles (33) are arranged displaceably in respect to the spinning

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electrode (31) and to the corresponding counter electrode (32) of the corresponding pair of counter electrodes (32).

- 16. A device according to any of Claims 11 to 15, **characterized in that** the direction of the mouth of air nozzles (33) is adjustable.
- 17. A device according to any of Claims 11 to 16, **characterized in that** the collecting place (4) of nanofibers (5) is composed of a sucking and collecting device (43) of nanofibers (5).

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- 18. A device according to any of Claims 11 to 16, **characterized in that** the collecting place (4) is composed of a collecting electrode (41) connected to a high voltage source of opposite polarity than the spinning electrode (31), whereby arranged in front of the collecting electrode (32) in a direction away from the spinning electrode (31) is a substrate material (2) or a means of depositing nanofibres. (5).
- 19. A device according to any of Claims 11 to 16, **characterized in that** the collecting place (4) is composed of a corona electrode (42) connected to a high voltage source of opposite polarity than the spinning electrode (31), whereby in front of the corona electrode (42) in a direction away from the spinning electrode (31) is out of contact with the corona electrode (42) arranged substrate material (2) or a means of depositing nanofibers (5).
- 20. A device according to any of Claims 13 to 19, **characterized in that** in the auxiliary spinning chamber (3) there is arranged at least one auxiliary nozzle (34) for feeding the supplementary gas.
- 21. A device according to any of Claims 11 to 20, **characterized in that** the collecting place (4) of nanofibers (5) is arranged above the spinning electrode (31) and the corresponding pair of counter electrodes (32) and the produced nanofibers (5) are carried in an upward direction to the collecting place (4) of nanofibers (5).
- 22. A device according to any of Claims 11 to 21, **characterized in that** the collecting place (4) of nanofibers (5) is arranged under the spinning electrode (31) and the corresponding pair of counter electrodes (32) and the

produced nanofibers (5) are carried to the collecting place (4) of nanofibers (5) in a downward direction.

23. A device according to Claim 21 or 22, **characterized in that** it is turned by an angle of up to 90° in any direction.

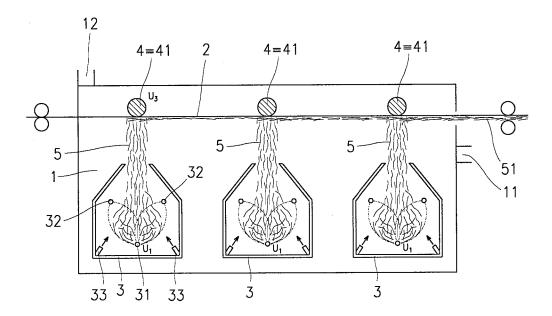


Fig. 1

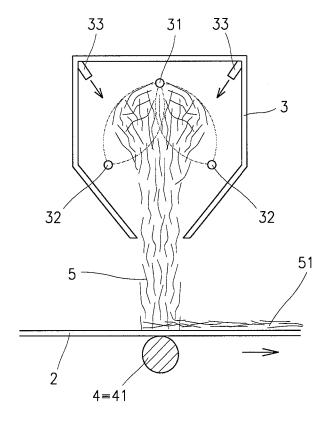


Fig. 2

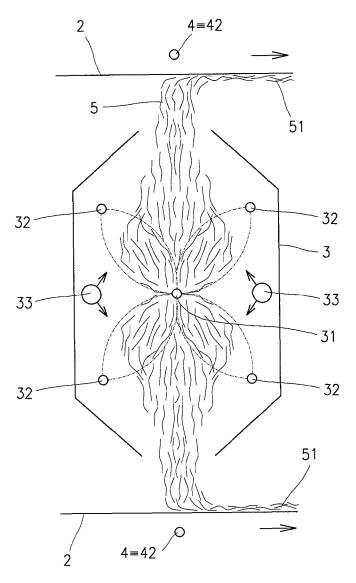
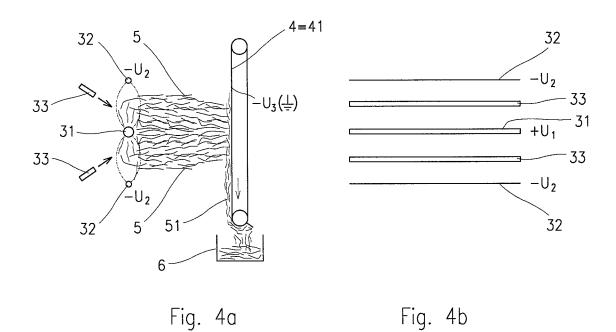


Fig. 3



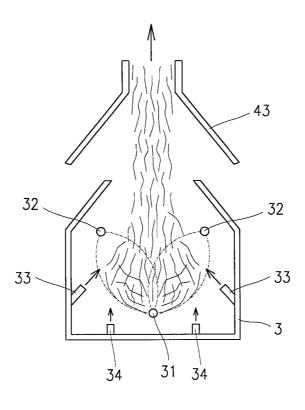


Fig. 5

#### INTERNATIONAL SEARCH REPORT

International application No PCT/CZ2013/000147

a. classification of subject matter INV. D01D5/00

ADD.

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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUM	ENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Х	US 2006/138711 A1 (BRYNER MICHAEL A [US] ET AL BRYNER MICHAEL ALLEN [US] ET AL) 29 June 2006 (2006-06-29) paragraphs [0013] - [0023]; figure 2	1-8, 10-20, 22,23
Х	US 2006/138710 A1 (BRYNER MICHAEL A [US] ET AL) 29 June 2006 (2006-06-29) paragraphs [0016] - [0027]; figure 2	1-6,8, 10-17, 20,22,23
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	column 7, line 31 - column 8, line 44; figures 1,2 column 9, lines 23-65	1/ 21,23

Further documents are listed in the continuation of Box C.	X See patent family annex.	
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"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family	
Date of the actual completion of the international search	Date of mailing of the international search report	
18 February 2014	25/02/2014	
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, Fax: (+31-70) 340-3016	Malik, Jan	

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