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

(11) EP 1 591 569 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
02.11.2005 Bulletin 2005/44

(51) Int Cl.^{7}: **D01F 2/00**, D01D 5/00

(21) Application number: **04460033.6**

(22) Date of filing: **26.07.2004**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PL PT RO SE SI SK TR
Designated Extension States:
AL HR LT LV MK

(30) Priority: **30.04.2004 PL 36760004**

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(54) Process for the production of nanofibres

(57) Process for the production of nanofibres with a diameter below 500 nm, consists in preparing a spinning solution of a natural polymer in a non-volatile solvent, feeding this solution by means of a metallic capillary linked to a current source to electrostatic field, in which the solution is converted into fibres, transporting the formed fibres on the surface of the flowing bath and finally collecting the coagulated fibres in a known way on a rotating drum or a tape stretched on rotating rollers. Electrostatic field is generated between the feeding capillary and a placed under it flowing coagulating bath linked to earth.

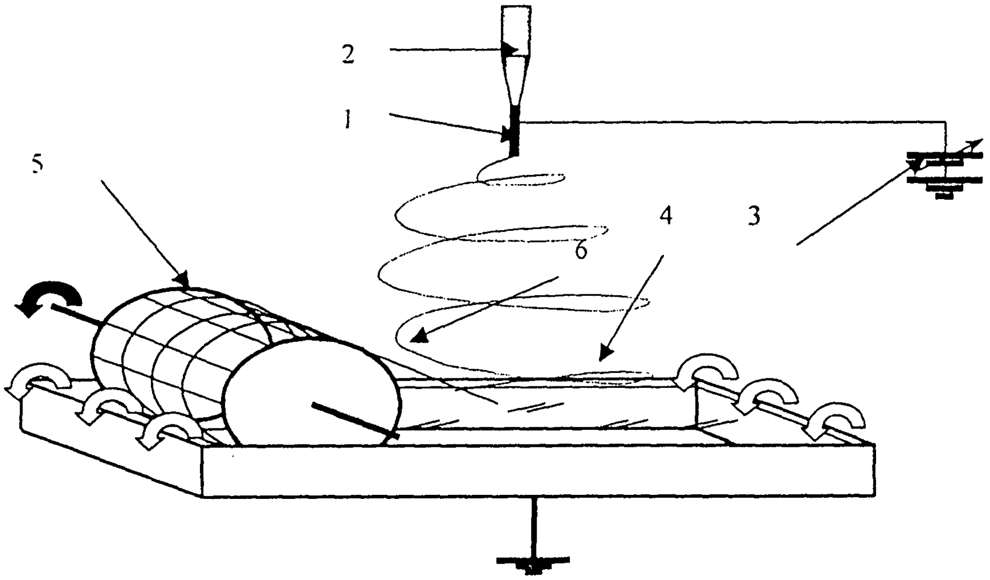

Fig. 2

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Description

[0001] The subject of the present invention is a process for the production of nanofibres with a diameter below 500 nm, in electrostatic field.

[0002] A process for the formation of fibres from a spinning solution of cellulose acetate in the mixture of acetone and ethyl alcohol in electrostatic field is known from Patent Specification U.S. 1 975 504. The spun fibres are collected on a moving metallic tape.

[0003] There are known processes for the production of nanofibres with a diameter below 500 nm from synthetic polymers consisting in preparing a spinning solutions of synthetic polymers in organic and inorganic volatile solvents and feeding it by means of a metallic or glass capillary, linked to a current source, onto earthed electrodes with various shapes placed in some distance from the capillary. The polymer solution flowing out from the capillary is drawn in electrostatic field between the capillary and the earthed electrode. The solvent is evaporated during fibre spinning, while the resultant fibres are deposited on the earthed electrode in the form of a non-woven. These processes are known from the following Patent Specifications: U.S. 4 345 414, U.S. 6 106 913, WO 2004/016839A1, U.S. 4 689 186, U.S. 4 323 525 as well as from the journals: Polymer 42, 9955-99667 (2001) and Journal of Electrostatics 35, 151-160 (1995).

[0004] There are also known processes for the production of nanofibres with a diameter below 500 nm from melted polymers consisting in feeding polymer melt by means of a metallic capillary linked to a current source to electrostatic field between the capillary and the earthed electrode. The melt is drawn in electrostatic field to form a stream that during cooling is solidified in the form of fibres deposited on the earthed electrode. These processes are described in Journal of Polymer Science: Polymer Physics Edition 1981, 19, 909-940.

The above processes of fibre formation in electrostatic field concern fibres spun from polymer solutions in readily volatile solvents or from melted polymers.

[0005] There is also known from Patent Application P-362101 a process for the production of nanofibres from solutions of natural polymers in non-volatile solvents, preferably from cellulose solution in N-methylmorpholine-N-oxide, in electrostatic field generated between a metallic capillary, feeding the spinning solution, linked to a current source, and an earthed electrode placed under it or between an electrode linked to a current source and, place inside the feeding capillary and the earthed electrode. Nanofibres formed in electric field from polymer solutions in non-volatile solvents contain large quantities of solvent and show a strong tendency towards sticking and changing shape.

[0006] The process for the production of nanofibres with a diameter below 500 nm, consisting in preparing a spinning solution of natural polymer in a non-volatile solvent, especially of cellulose in N-methylmorpholine-N-oxide, feeding this solution by means of a metallic capillary, linked to a current source, to electrostatic field in which fibres are formed from the solution, winding the resultant fibres onto a take-up device, according to the present invention, is characterised by the fact that these fibres are formed in electrostatic field generated between a feeding capillary and placed under it moving coagulation bath linked to earth, followed by transporting the formed fibres on the surface of the moving coagulation bath to remove the non-volatile solvent and to solidify the fibres, which are finally taken-up in a usual way by a rotating drum or a tape moving on rotating rollers. As a coagulation bath, water containing an addition of a surface-active agent is preferably used, and besides as a coagulation bath there is used water, water with an addition of solvent, volatile solvents.

[0007] In a modification of the process according to the invention, fibres are formed in electrostatic field generated between a feeding capillary and placed under it, rotationally mounted, metallic structure linked to earth. The formed fibres are led into a space between elements of this structure, where fibres are subjected to the coagulating action of a hot steam stream and finally the coagulated fibres are taken up.

[0008] In a further modification of the process according to the invention, fibres are formed in electrostatic filed generated between a feeding capillary and moving under it woven fabric, beneath which is placed an earthed and cooled electrode. The formed fibres are directed onto the moving fabric, where they are coagulated with a hot stream of steam first and then with a water stream that rinses off the solvent; finally, the coagulated fibres are taken up.

[0009] The nanofibres produced by the process according to the present invention contain no solvent and show no tendency towards sticking and changing shape.

[0010] The process according to the invention is illustrated by the below given examples with reference to Figures from 1 to 14 that show the schemes of equipment an fragments of equipment used to form the fibres in particular examples. The parts mentioned in the examples mean parts by weight.

Example I.

[0011] A spinning solution was prepared from 1 part of cellulose with a degree of polymerisation (DP) of about 800 in 35 parts of N-methylmorpholine-N-oxide (NMMO) and 6.5 parts of water with 0.1 parts of a stabiliser. This solution was placed in container 2 of the feeding device shown in Fig. 1, heated to 105°C, terminated with a metallic capillary 1 with a diameter of 0.4 mm linked to current source 3 under a voltage of 6 kV. The solution was fed by means of capillary 1 to electrostatic field generated between capillary 1 and placed under it earthed tub 4 containing a coagulating bath. The distance between capillary 1 and bath 4 was 10 cm. The stream of polymer solution drawn in electrostatic field and cooled was directed onto the surface of coagulation bath 4 consisting of water with an addition of a surface-active agent at a temperature of 10°C. In bath 4, the solvent is rinsed off and fibres are solidified. The reduced rate of taking off fibres from bath 4 brings about the formation, on its surface, of a cellulose film composed from fibres with a thickness of 150 nm.

Example II.

[0012] A spinning solution was prepared from 1 part of cellulose with a DP of about 800 in 16.0 parts of NMMO and 3.0 parts of water with 0.1 part of a stabiliser. This solution was placed in container 2 of the feeding device shown in Fig.2, heated to 125°C, terminated with metallic capillary 1 with a diameter of 0.6 mm linked to current source 3 under a voltage of 17 kV. The solution was fed be means of capillary 1 into electrostatic field generated between capillary 1 and placed under it earthed tub with flowing through it coagulating bath 4. The tub was equipped with rotating drum 5. The distance between capillary 1 and bath 4 was 12 cm. The drawn in electrostatic field and cooled stream of polymer solution was directed onto the surface of flowing coagulation bath 4 consisting of water containing a surface-active agent, cooled down to a temperature of 5°C. In bath 4, the solvent was rinsed off and fibres were solidified. Then, the formed fibres in the form of tow 6 were wound on drum 5 pulling the fibres out from the surface of bath 4, which prevented the formation of cellulose film on the surface of bath 4.
The produced nanofibres showed a thickness of 70 nm.

Example III.

[0013] A spinning solution was prepared from 1 part of cellulose with a DP of about 800 in 30.4 parts of NMMO and 3.1 parts of water with 0.1 part of a stabiliser. The solution was placed in contained 2 of the feeding device shown in Fig. 3, heated to a temperature of 116°C, terminated with metallic capillary 1 with a diameter of 0.8 mm, linked to current source 3 under a voltage of 19 kV. The solution was fed by means of capillary 1 into electrostatic field generated between capillary 1 and placed under it tub 5 containing coagulation bath 4. The distance between capillary 1 and bath 4 was 8 cm. In the bottom of bath 5 containing bath 4 was made hole 6 with attached to its edges earthed discharging stub pipe 7 (Fig. 4) that was cone-shaped in its upper part and its lower part was a section of pipe with a diameter of 1 cm. On the internal surface of discharging stub pipe 7 a spiral guide was made. Drum 8 rotating both around its axis of rotation and along this axis was placed under stub pipe 7. The drawn in electrostatic field and cooled stream of polymer solution was directed onto the surface of coagulating bath 4 consisting of water containing a surface-active agent, cooled to a temperature of 25°C. In bath 4 the solvent was rinsed off and fibres were solidified, and then the formed nanofibres with bath 4 flowed out into discharging stub pipe 7, in which they were twisted into a thread with a thickness of 1 cm by the guide and wound uniformly on drum 8.

Example IV.

[0014] Nanofibres were formed from the spinning solution prepared as in Example III, using the equipment as in Example III (Fig. 5) with a difference that the thread formed by means of the guide in stub pipe 7 was taken up on tape 9 stretched on two rollers moving both around and along the rotation axis.

Example V.

[0015] A spinning solution was prepared from 1 part of cellulose with a DP of about 800 in 35.5 parts of NMMO and 6.5 parts of water containing 0.1 parts of stabiliser and 0.2 parts of fullerenes. The solution was placed in container 2 of the feeding device shown in Fig. 6, heated to a temperature 115°C, terminated with metallic capillary 1 with a diameter of 0.9 mm, linked to current source 3 under a voltage of 17 kV. The solution was fed by means of capillary 1 into electrostatic field generated between capillary 1 and placed under it earthed tub 4 with coagulating bath 5 flowing through it. The distance between capillary 1 and bath 5 was equal to 8 cm. The stream of polymer solution, drawn in electrostatic field and cooled, was directed onto the surface of flowing through tub 4 coagulating bath 5 in the form of a thin film of water containing a surface-active agent, at a temperature of 20°C, in which the solvent was rinsed off and fibres were solidified. The resultant nanofibres, together with bath 5 flowed out from tub 4 on the surface of rotating drum 6.
The produced nanofibres showed a thickness of 290 nm.

Example VI.

[0016] Nanofibres were formed from a spinning solution prepared as in Example V, in the equipment as in Example V (Fig. 7) with the difference that the produced fibres together with bath 5 flowed out from tub 4 onto the surface of tape 6 stretched on two rotating rollers.

Example VII.

[0017] A spinning solution was prepared from 1 part of cellulose with a DP of about 800 in 35.5 parts of NMMO and 6.5 parts of water containing 0.1 part of stabiliser. The solution was placed in container 2 of the feeding device shown in Fig. 8, heated to a temperature of 95°C, terminated with metallic capillary 1 with a diameter of 0.4 mm linked to current source 3 under a voltage of 8 kV. The solution was fed by means of capillary

1 into electrostatic field generated between capillary 1 and a stainless steel structure placed under it. This structure consisted of two perpendicular frames 4 placed one in the other and linked to earth. The distance between capillary 1 and frames 4 was equal to 15 cm. The stream of polymer solution drawn in electrostatic field and cooled was directed to the metallic structure and coagulated with hot steam 5 that removed the solvent and solidified the fibres. Steam was discharged from the space of fibre formation through offtake 6. The solidified fibres were taken up by means of devices shown in Fig. 9.
The produced nanofibres showed a thickness of 160 nm.

Example VIII.

[0018] A spinning solution was prepared from 1 part of cellulose with a DP of about 800 in 35.5 parts of NMMO and 6.0 parts of water containing 0.1 part of stabiliser. The solution was placed in container 2 of the feeding device shown in Fig. 10, heated to a temperature of 98°C, terminated with metallic capillary 1 with a diameter 0.4 mm linked to current source 3 under a voltage of 11 kV. The solution was fed by means of capillary 1 into electrostatic field generated between capillary 1 and placed under it stainless steel structure composed of two rotating rings 4 situated in parallel and linked to earth. The distance between capillary 1 and rings 4 was equal to 16 cm. The stream of polymer solution drawn in electrostatic field and cooled was directed onto the metallic structure and coagulated by hot steam 5 that removed the solvent and solidified the fibres, which were deposited within the space between rings 4 (Fig. 11). Steam was discharged from the space of fibre formation through offtake 6.
The produced nanofibres showed a thickness of 120 nm.

Example IX.

[0019] Nanofibres were formed from a spinning solution as in Example VIII proceeding as in Example VII with the difference that the stainless steel structure used was composed of three rings situated in parallel and four rings situated in parallel (Fig. 12).

Example X.

[0020] A spinning solution was prepared from 1 part of cellulose with a DP of about 800 in 26.5 parts of NMMO and 6.0 parts of water containing 0.1 parts of stabiliser and 0.18 parts of silica nanoparticles with a grain diameter of 9 nm. This solution was placed in container 2 of the feeding device shown in Fig. 13, heated to a temperature of 105°C, terminated with metallic capillary 1 with a diameter of 0.4 mm, linked to current source 3 under a voltage of 27 kV. The solution was fed by means of capillary 1 into electrostatic field generated between capillary 1 and moving under it fabric 4, under which earthed and cooled electrode 5 was placed. The distance between capillary 1 and fabric 4 was equal to 12 cm. The stream of polymer solution drawn in electrostatic field and cooled was directed onto moving fabric 4, on which it was coagulated first with hot steam stream 6 and then with stream 7 of rinsing solvent NMMO. The space of fibre formation was separated from the steam blow-in zone with impermeable screen 8.
The produced nanofibres showed a thickness of 150 nm.

Example XI.

[0021] A spinning solution was prepared from 1 part of cellulose with a DP of about 800 in 35.5 parts of NMMO and 6.5 parts of water containing 0.1 parts of stabiliser and 0.15 parts of Fe_3O_4 with a grain diameter of 9nm. This solution was placed in container 2 of the feeding device shown in Fig. 14, heated to a temperature of 109°C, terminated with metallic capillary 1 with a diameter of 0.6 mm, linked to current source 3 under a voltage of 12 kV. The solution was fed by means of capillary 1 into electrostatic field generated between capillary 1 and placed under it tub with flowing coagulating bath 4 composed of water and a surface-active agent cooled to a temperature of 23°C. Under the surface of bath 4, earthed ring 5 was placed. The distance between capillary 1 and bath 4 was equal to 7 cm. The stream of polymer solution drawn in electric field and cooled was directed onto the surface of coagulating bath 4 flowing through the tub where the solvent was rinsed off and the fibres were solidified. The fibres formed on the surface of bath 4 were transported by means of rotating roller 6, placed under ring 5, onto roller 8 to take up the formed fibres in the form of tow 7. Rollers 6 and 8 rotated with a speed that ensured a continuous take-up of fibres from the surface of bath 4.
The produced nanofibres showed a thickness of 350 nm.

Claims

1. Process for the production of nanofibres with a diameter below 500 nm, consisting in preparing a spinning solution of a natural polymer in a non-volatile solvent, especially cellulose in N-methylmorpholine-N-oxide, feeding this solution by means of a metallic capillary linked to a current source to electrostatic field, in which the solution is converted into fibres, winding the resultant fibres on a take-up device, **characterised in that** the fibres are formed in electrostatic field generated between the feeding capillary and a placed under it flowing coagulating bath linked to earth, followed by transporting the formed fibres on the surface of the flowing bath and

finally collecting the coagulated fibres in a known way on a rotating drum or a tape stretched on rotating rollers.

2. Process according to claim 1, **characterised in that** as a coagulating bath there is preferably used water containing an addition of a surface-active agent, and besides as a coagulating bath there is used water, water with an addition of solvent, volatile solvents.

3. Process for the production of nanofibres with a diameter below 500 nm, consisting in preparing a spinning solution of a natural polymer in a non-volatile solvent, especially cellulose in N-methylmorpholine-N-oxide, feeding this solution by means of a metallic capillary linked to a current source to electrostatic field, in which the solution is converted into fibres, winding the resultant fibres on a take-up device, **characterised in that** the fibres are formed in electrostatic field generated between the feeding capillary and a placed under it rotating metallic structure linked to earth, followed by directing the formed fibres into the space between the elements of this structure where fibres are coagulated with a stream of hot steam and finally taken up.

4. Process for the production of nanofibres with a diameter below 500 nm, consisting in preparing a spinning solution of a natural polymer in a non-volatile solvent, especially cellulose in N-methylmorpholine-N-oxide, feeding this solution by means of a metallic capillary linked to a current source to electrostatic field, in which the solution is converted into fibres, winding the resultant fibres on a take-up device, **characterised in that** the fibres are formed in electrostatic field generated between the feeding capillary and a moving under it woven fabric, under which is placed an earthed cooled electrode, followed by directing the formed fibres on the moving fabric where they are coagulated with a stream of hot steam first and then with a stream of liquid that rinses the solvent off, the coagulated fibres being finally taken up.

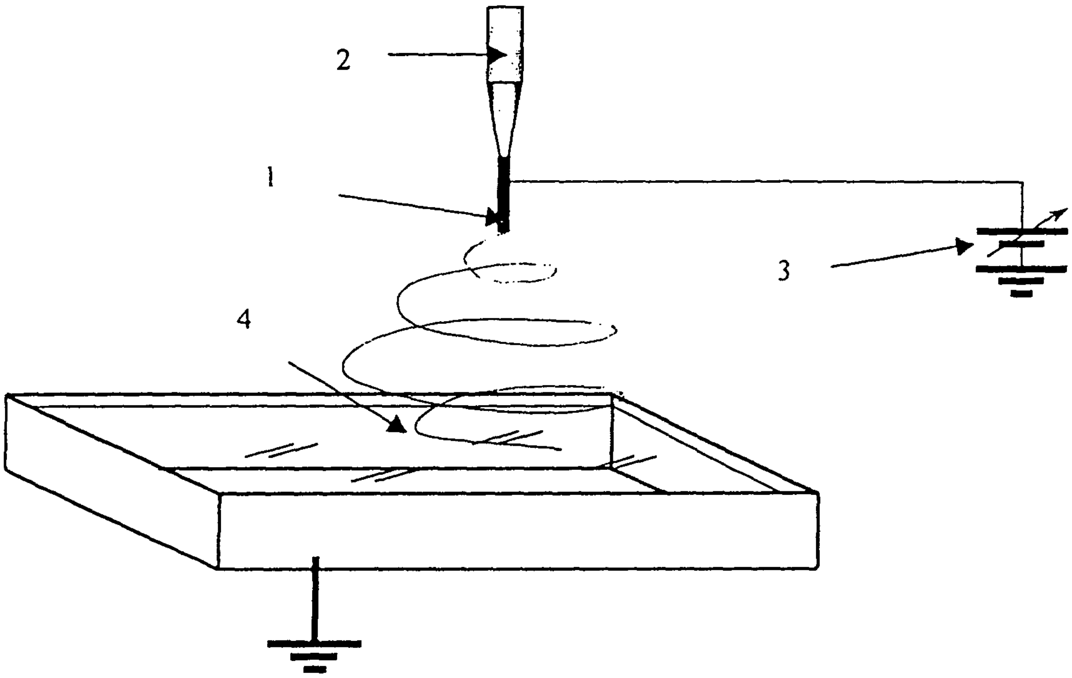

Fig. 1

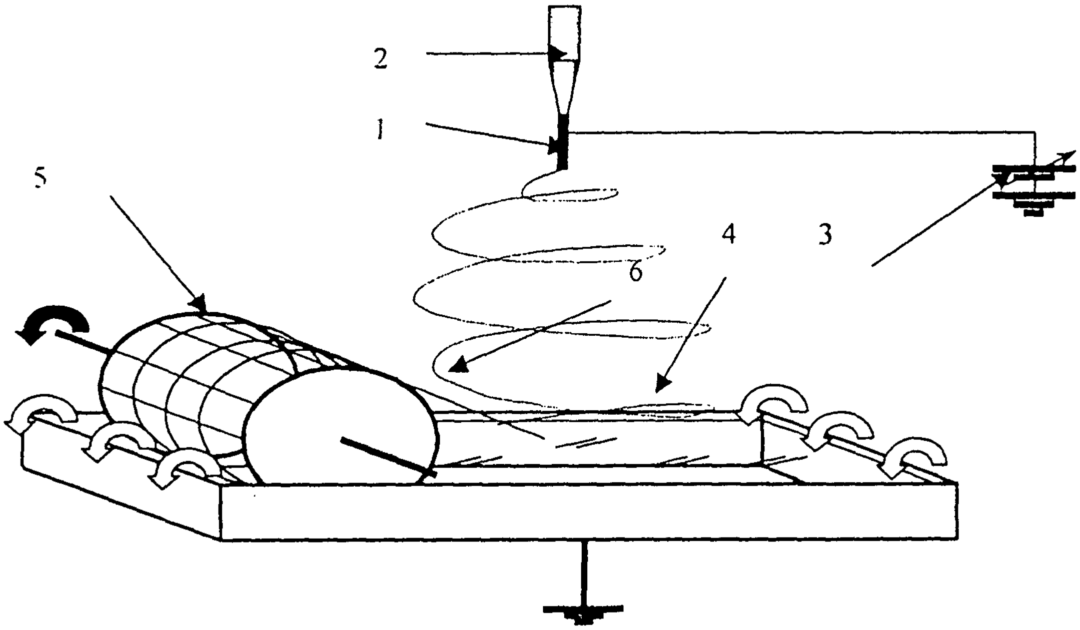

Fig. 2

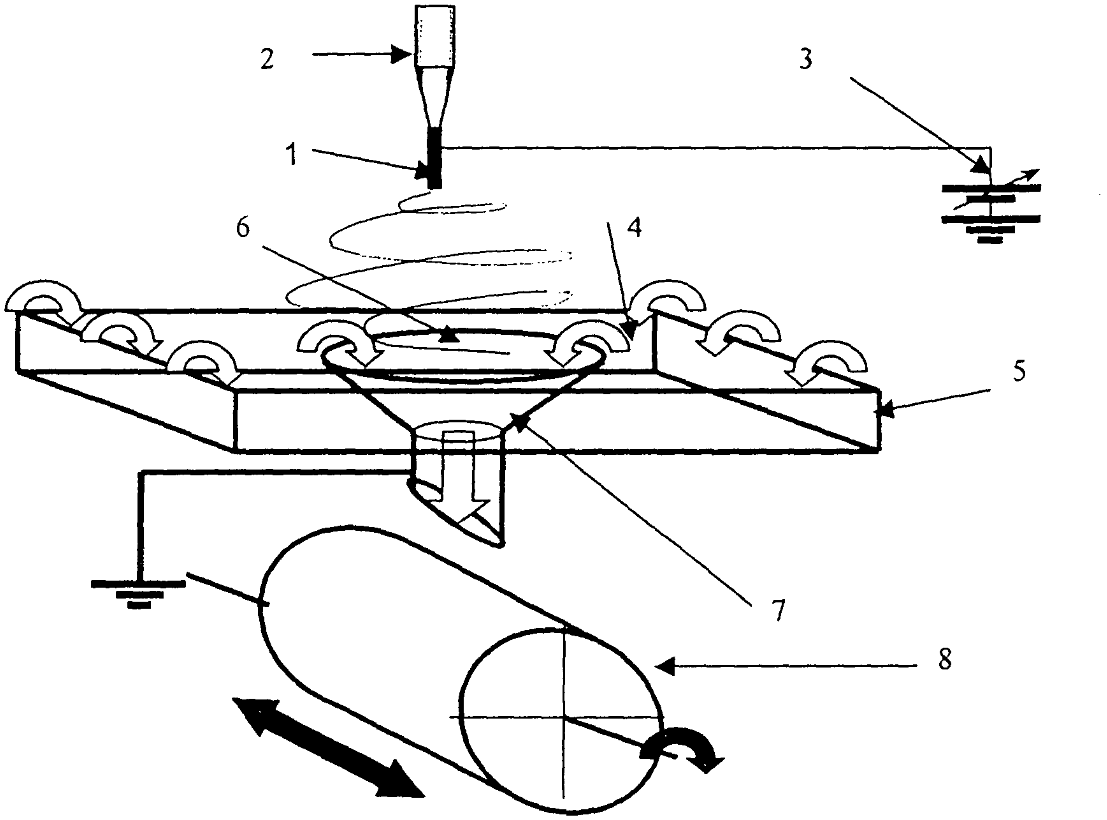

Fig. 3

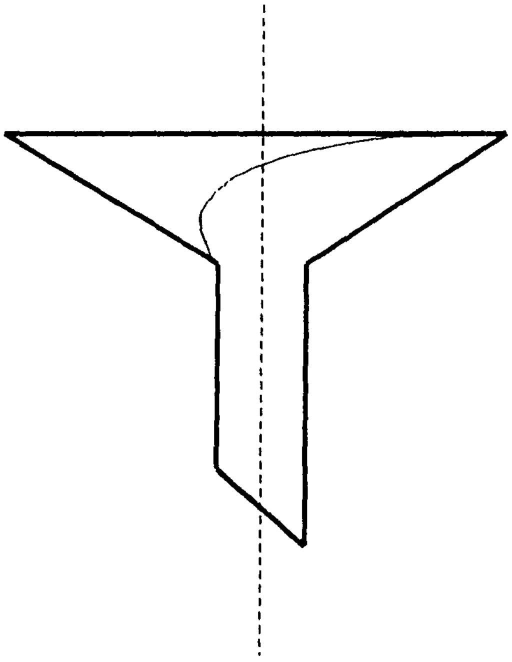

Fig. 4

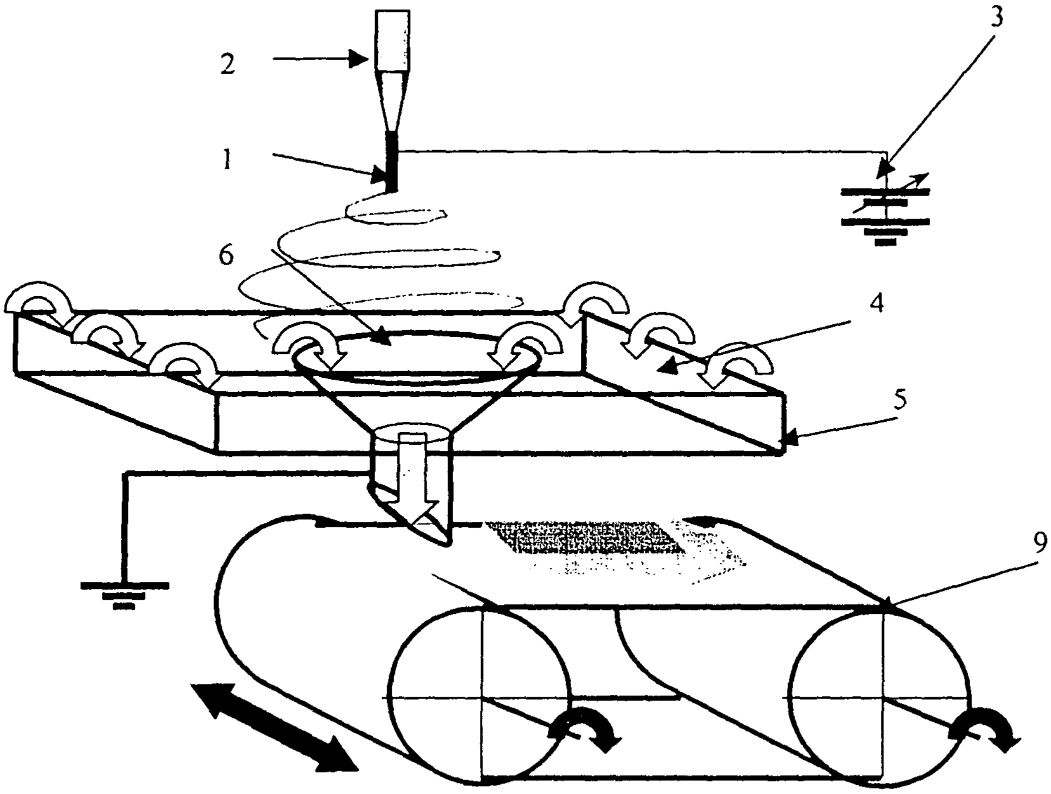

Fig. 5

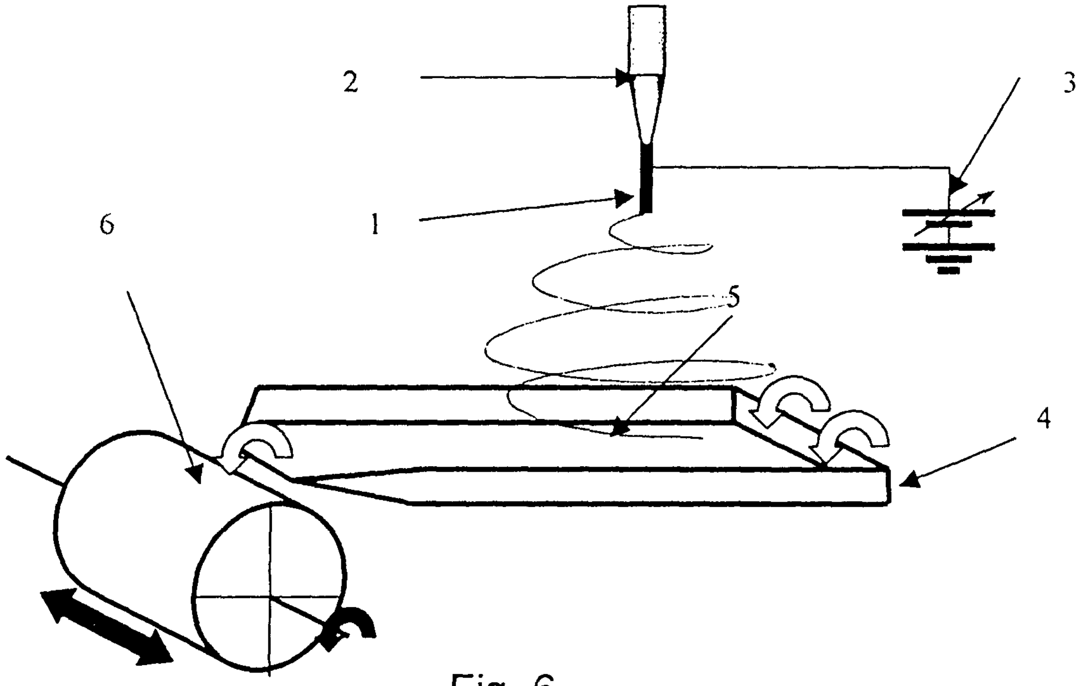

Fig. 6

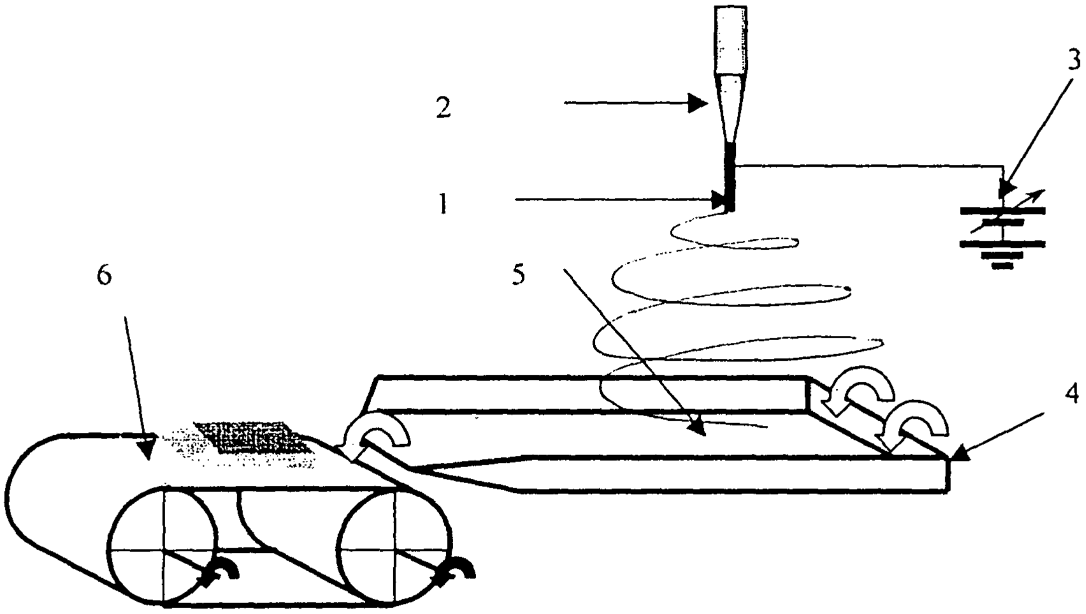

Fig. 7

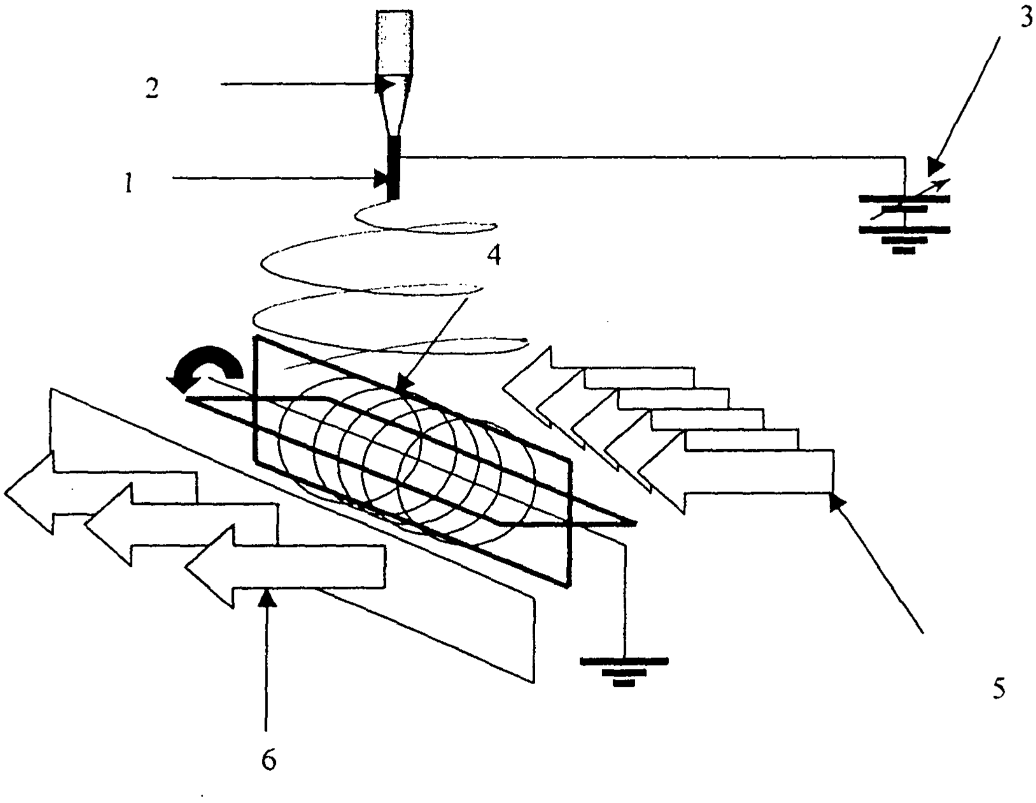

Fig. 8

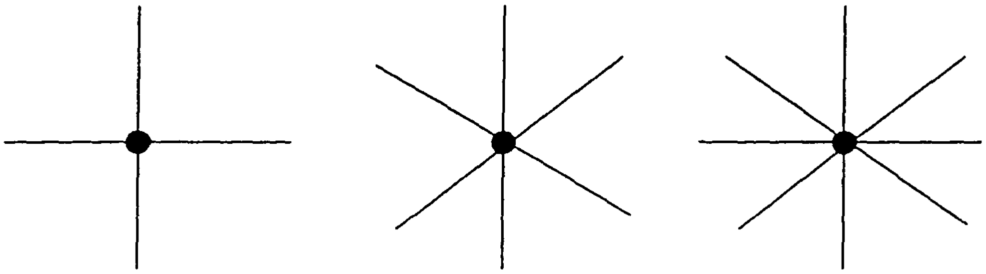

Fig. 9

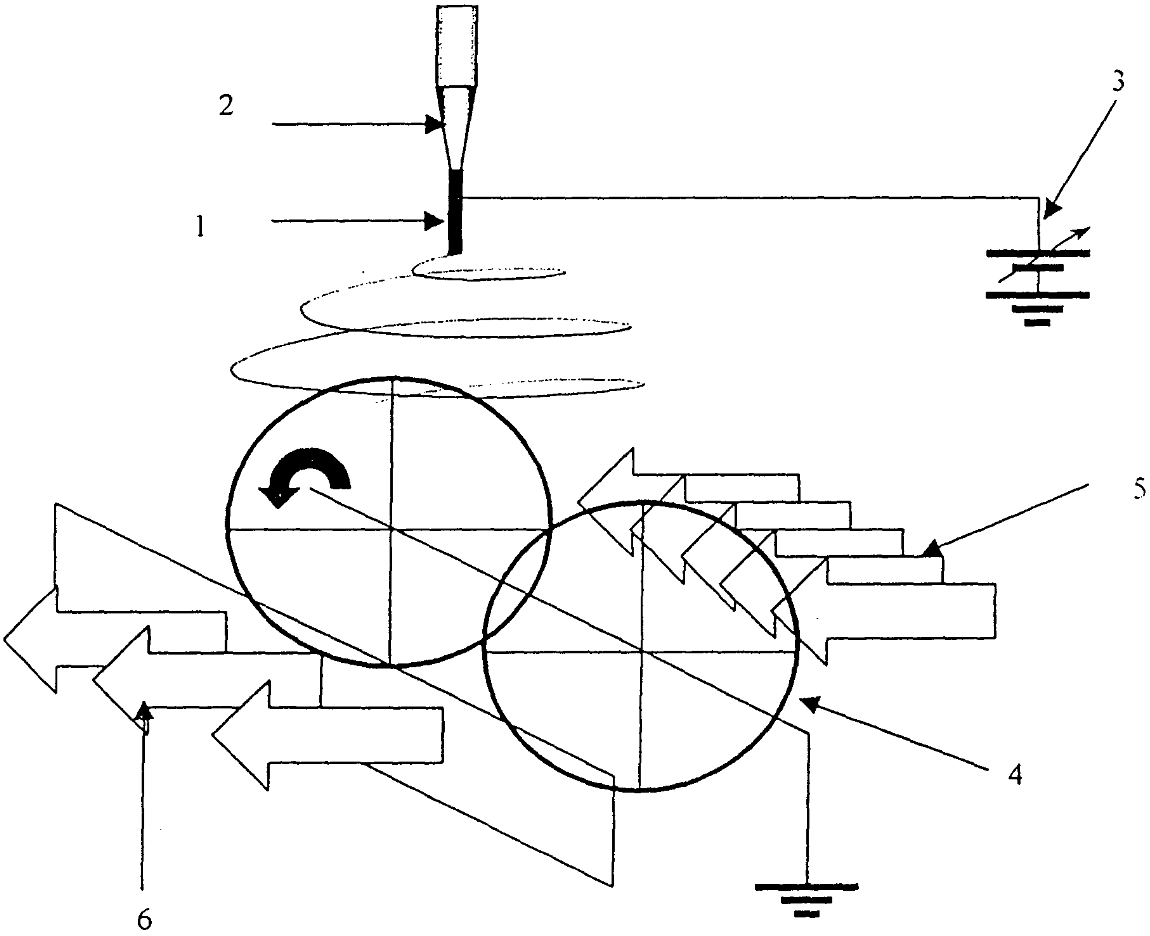

Fig. 10

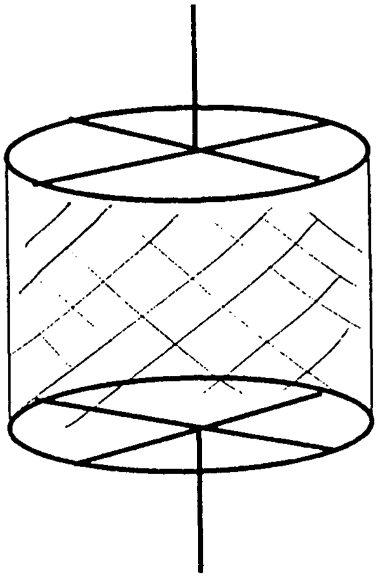

Fig. 11

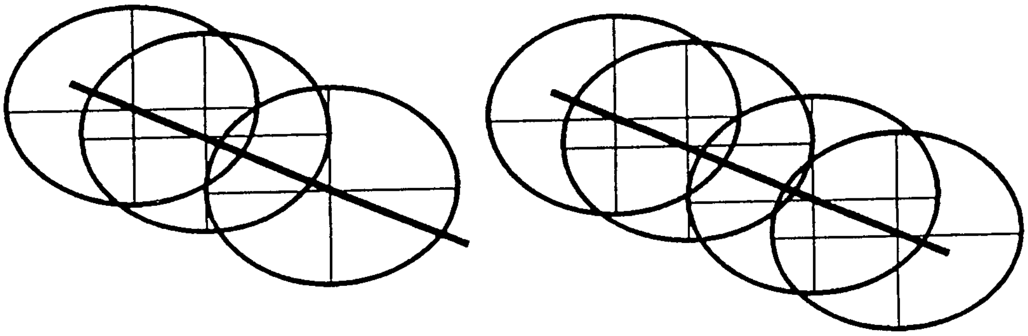

Fig. 12

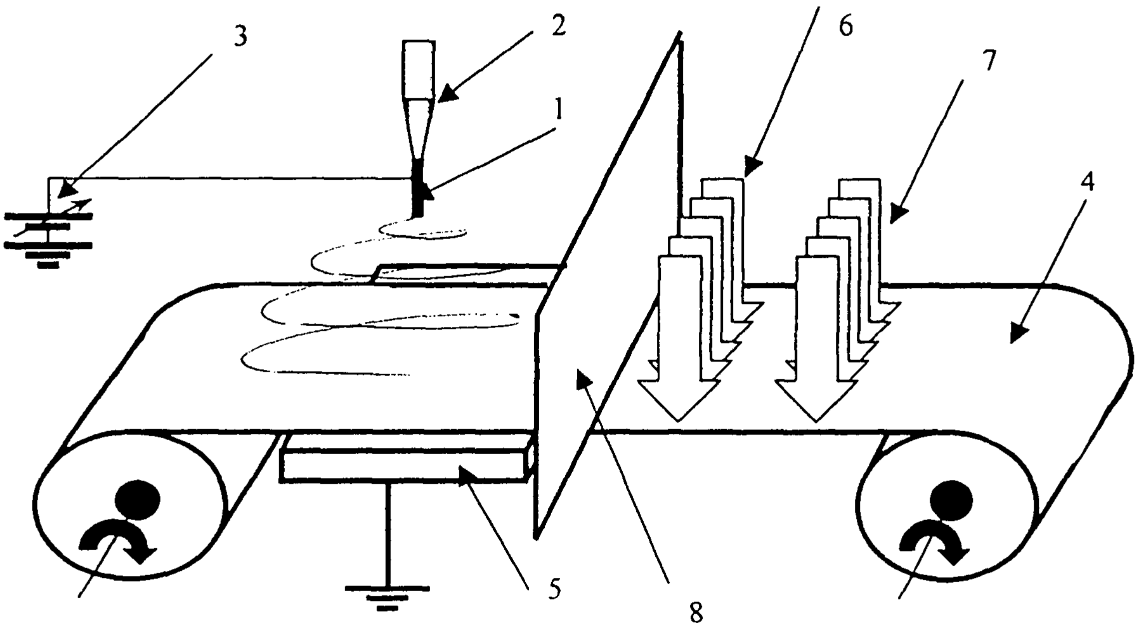

Fig. 13

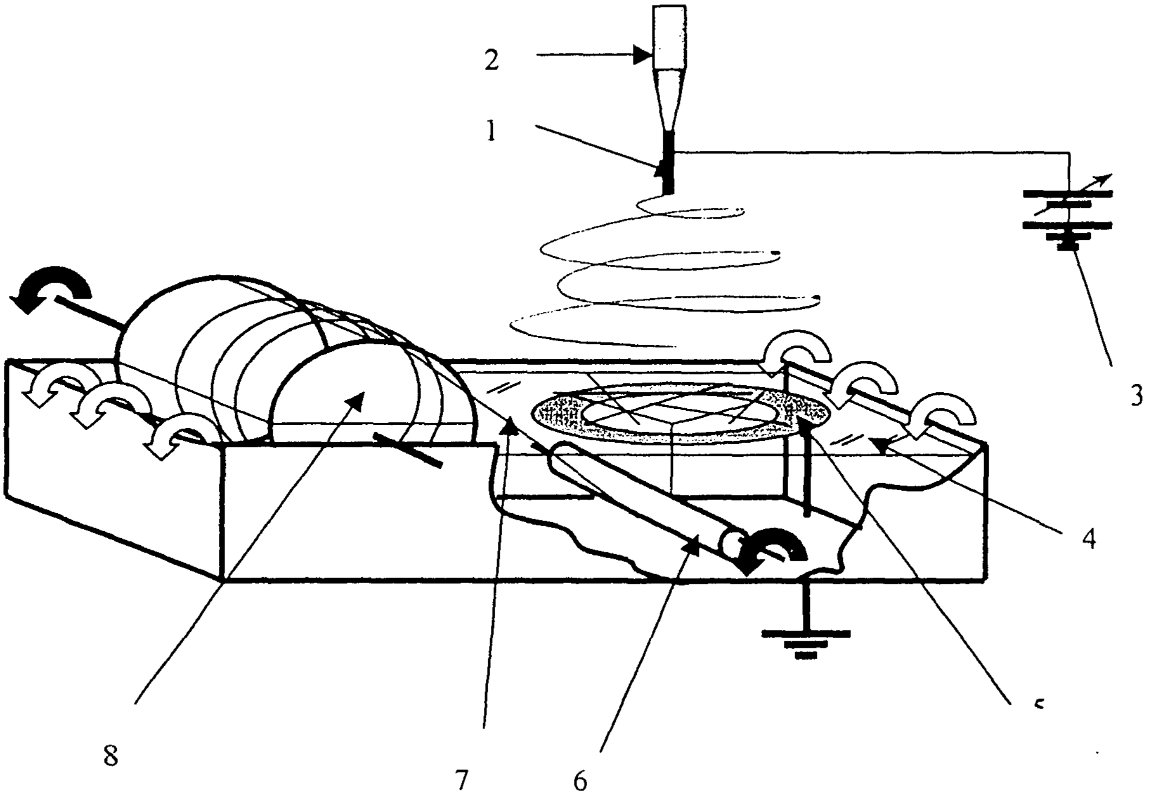

Fig. 14

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EUROPEAN SEARCH REPORT

Application Number
EP 04 46 0033

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	YOUNG SIC KANG ET AL: "MANUFACTURING THE CELLULOSE WEB BY USING ELECTRO-SPINNING AND IN-VITRO BEHAVIOUR OF OXIDIZED CELLULOSE WEG" HAN'GUG SEOMYU GONGHAG HOEJI-HAN'GUG SOMYU GONGHAGHOE - JOURNAL OF THE KOREAN FIBER SOCIETY, HAN'GUG SEOMYU GONGHAGHOE, SEOUL, KR, vol. 39, 2002, pages 14-20, XP008050645 ISSN: 1225-1089 * abstract; figure 1 * -----	1-4	D01F2/00 D01D5/00
A	ANONYMOUS: "The latest technology news and patent summaries" FILTRATION AND SEPARATION, CROYDON, GB, vol. 40, no. 10, December 2003 (2003-12), page 18, XP004481922 ISSN: 0015-1882 * column 2, line 9 - column 3, line 11 * -----	1-4	
D,A	US 1 975 504 A (FORMHALS ANTON) 2 October 1934 (1934-10-02) * column 4, line 117 - line 143; claims; figures * -----	1-4	TECHNICAL FIELDS SEARCHED (Int.Cl.7) D01F D01D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	9 August 2005	Tarrida Torrell, J

CATEGORY OF CITED DOCUMENTS

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 04 46 0033

09-08-2005

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