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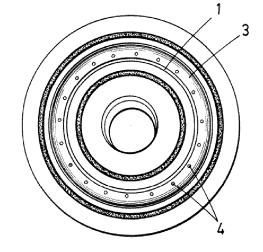
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(54) NOZZLE WITH MULTIPLE OUTLETS

(57) The invention relates to a nozzle with multiple outlets, comprising at least one chamber through which a fluid can flow, with a fluid inlet opening and a plurality of fluid outlet openings through which the fluid leaves the nozzle in optimum conditions for being acted upon electrohydrodynamically or aerohydrodynamically. The nozzle can be used with low-viscosity fluids as it comprises at least one fluid distributor (3) in the chamber, consisting

of a hollow body through which the fluid entering the chamber flows. The fluid distributor (3) allows the uniform distribution of the fluid through all of the outlet openings of the chamber, and prevents the fluid from only flowing out through the outlet openings closest to the inlet opening. The invention improves results relating to the production of microstructured, submicrostructured and nanostructured materials.





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OBJECT OF THE INVENTION

[0001] The present invention falls within the technical field of injection systems with multiple outlets for the production of microstructured, submicrostructured and nanostructured materials.

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[0002] More specifically, it relates to a multi-outlet nozzle that can be simple, coaxial or multiaxial and that enables working with low-viscosity fluids ensuring that said fluids leave through all the outlets of the nozzle.

BACKGROUND OF THE INVENTION

[0003] Electrohydrodynamic or aerohydrodynamic processing is a method for obtaining fibers, particles and/or capsules by means of the action of an outer electrical field that is applied between two electrodes and to which a dissolved or melted polymer is subjected. The two electrodes are an atomizing nozzle-tip through which the polymer is made to flow and a collecting electrode. [0004] The structures obtained through electrohydrodynamic or aerohydrodynamic processing are particles, fibers and/or capsules of micrometric, submicrometric and nanometric size. When dissolved polymers are used in this method it is not necessary to use temperature to eliminate the solvent that is used. In the case in which temperature is used to process those polymers that are used from a melted state, the process is called electrohydrodynamic processing of a melt, also known as melt electrospinning.

[0005] In electrohydrodynamic or aerohydrodynamic processing, as a result of the application of the electrical field, a stream of polymer solution or of a polymer melt to be atomized is expelled from the atomizing nozzle-tip (it can be a stream of one liquid or a melt or several). The stream is subsequently elongated and consequently the fibers, particles and/or capsules are formed by means of the evaporation of solvents or by solidification of the melt. [0006] The blow spinning/spraying technique consists in applying pressure differences in order to accelerate the liquid or liquids that flow through a nozzle-tip in order to obtain particles, fibers and/or capsules of micrometric, submicrometric and nanometric size.

[0007] Simple multiple-outlet nozzles are devices comprising two or more nozzle-tips arranged in an organized manner in order to improve the distribution of the flow of fluid, of the voltage and/or of applied gas.

[0008] Multiaxial nozzles with multiple outlets are devices comprising two or more special nozzle-tips through which two or more different liquids, melts or gases circulate at the same time in a concentric or parallel manner. [0009] These two types of nozzles enable increasing production levels for electrohydrodynamic or aerohydrodynamic processing since the productivity of single nozzle-tip equipment is very low and the workflow rate is typically limited to between 1 and 5 ml/hour and to 100

ml/hour at most.

[0010] From the state of the art, studies on using a filter that reduces repulsion between the fibers are known; it improves performance, lowers the diameter and improves uniformity of the fibers. A device has also been developed that is used to produce nanofibers with a high production rate and that comprises a spray nozzle-tip, a liquid storage chamber, a gas storage tube, a gas transportation tube and another tube for the transportation of the liquid.

[0011] It has also been demonstrated that using a twin screw extruder on the front portion of the electrospinning equipment provides capacities such as the transportation of solids, mixing of polymer resins and devolatilization and temperature control that would be feasible when working with relatively high flow rates and with nozzles with multiple needles.

[0012] From the state of the art, for example, it is known document US2008131615 that describes an electrohydrodynamic spraying and spinning deposition system for the production of nanofibers or droplets. It has a high voltage source that creates a high voltage potential applied between an array of spraying tips and the deposition surface.

[0013] A technical problem shared by the known devices of the state of the art for producing nanostructured materials with electrohydrodynamic or aerohydrodynamic processing, is that they cannot be used with low-viscosity fluids, such as liquid paraffins, alcohols, water etc. This is due to the fact that the rheological properties of the low-viscosity fluids, when the fluid descends through the outlets, cause the flow rate of the fluids to be too high for electrohydrodynamic or aerohydrodynamic processing. The consequence of this is that the outlet of the fluid, which is in the nozzle, is carried out by only half or a third of the outlets of said nozzle. The generated product is defective.

DESCRIPTION OF THE INVENTION

[0014] The present invention proposes a multi-outlet nozzle that can be simple, coaxial or multiaxial and in which the injection is produced at the outlets. The nozzle is intended for the production of microstructured, submicrostructured and nanostructured materials.

[0015] The nozzle enables producing fibers, particles and/or capsules on a micrometric, submicrometric and nanometric scale through electrohydrodynamic or aerohydrodynamic processing like electrospinning, electrospraying, melt electrospinning and blow spinning and spraying. The nozzle can also be used in uniaxial, coaxial or multiaxial electrohydrodynamic or aerohydrodynamic processes, these fluids being able to flow in a coaxial or parallel manner.

[0016] The present invention solves the problem of the nozzles in the state of the art that cannot be used with low-viscosity fluids because defective products are generated. An example of a low-viscosity fluid to act as a

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reference is water, which has a viscosity of 1 centipoise at 20°-C.

[0017] The key of the nozzle of the present invention is that it comprises a fluid distributor that allows decreasing the speed of the fluid and distributing it homogeneously in all the nozzle outlets.

[0018] It enables obtaining more uniform fibers (it decreases the variability of the diameter of the fibers), it is more efficient in terms of applied electrical fields and it allows for better control of the design of the obtained material.

[0019] In an example of a nozzle with concentric emitters (with two needles) said nozzle comprises the following elements: an outer needle and an inner needle, an outer chamber and an inner chamber, an inner fluid inlet duct and an outer fluid inlet duct. The number of emitters is not limiting, there could be more than two.

[0020] The nozzle comprises at least one fluid distributor, which is the element that achieves an even distribution of the low-viscosity fluid towards all the outlets of the nozzle. The distributor can be in any of the chambers of the nozzle whether it is uniaxial, coaxial or multiaxial (the uniaxial nozzle has a single chamber, the coaxial nozzle has two chambers and the multiaxial nozzle has two or more chambers). Thus, the fluid distributor can be used for the internal fluid, for the external fluid(s) or for all the fluids at the same time depending on where it is arranged.

[0021] In the nozzles of the state of the art, when the fluid enters the corresponding chamber it flows to the needles preferably falling through the needles closest to the injection inlet. This is what causes the poor results of the nozzles that were described previously. However, when the fluid distributor is installed in the chambers of the nozzle, the fluid enters the fluid distributor first and then flows to the needles.

[0022] The fluid distributor is a hollow body with a configuration corresponding to the chamber of the nozzle in which it will be installed. The distributor can be made of any material that is not soluble in the components of the solution that will be introduced into the nozzle. In an exemplary embodiment, the fluid distributor can be made of a porous material that can be metallic, plastic and/or ceramic, which also allows for a homogeneous flow to circulate through each of the nozzle-tips. If a porous material is used, it causes a drop in pressure in the flow of the liquid, obtaining a similar result to when a fluid distributor of nonporous material is used with the advantage that it can be used for both low-viscosity liquids and viscous liquids. The porosity of the material can be designed depending on the viscosity of the fluid that is going to pass through the fluid distributor.

[0023] The use of porous materials for the production of the fluid distributor enables making multi-outlet nozzles with fluid distributor in which each fluid flows through the fluid distributor in the corresponding chamber having a material with different porosity depending on the viscosity of the fluid that will cross through it. This will ensure a

better distribution of the fluid depending on its viscosity.

DESCRIPTION OF THE DRAWINGS

[0024] As a complement to the description provided herein and for the purpose of helping to make the characteristics of the invention more readily understandable, in accordance with a preferred practical embodiment thereof, said description is accompanied by a set of drawings constituting an integral part of the same, which by way of illustration and not limitation represent the following:

Figure 1. - Shows a view of a fluid distributor.

Figure 2. - Shows a view of the internal fluid chamber of a nozzle with the fluid distributor.

Figure 3. - Shows a perspective view of a coaxial or multiaxial nozzle with multiple outlets.

Figure 4. - Shows an image of the morphology of polyvinylpyrrolidone and RT5 fibers obtained through coaxial electrohydrodynamic or aerohydrodynamic processing using a multi-outlet nozzle as described.

Figure 5. - Schematic view of a porous material that enables distributing the fluid uniformly through several outlets.

PREFERRED EMBODIMENT OF THE INVENTION

[0025] What follows is a description of an exemplary embodiment of the invention with reference to Figures 1 to 5.

[0026] A multi-outlet nozzle is proposed of the type comprising at least one chamber for the flowing of a fluid. Said chamber in turn comprises an inlet opening connected to a fluid inlet duct and a plurality of outlet openings through which the fluid leaves the nozzle.

[0027] The key of the nozzle of the present invention is that it comprises a fluid distributor (3), arranged in the chamber, which is a hollow body intended for the flow of the fluid crossing said chamber and having a configuration corresponding to the geometry of the interior of the chamber (1, 2), and it is connected to a first opening that is an inlet opening for allowing the flow of the fluid therein and comprises a plurality of second openings (4) aligned with the outlet openings of the chamber (1, 2) for allowing the outlet of the flow crossing it, through the outlet openings in a uniform manner.

[0028] In an exemplary embodiment of the invention the nozzle comprises two or more chambers (1, 2) and comprises a fluid distributor (3) in at least one of the chambers.

[0029] In this case, the nozzle comprises at least one inner chamber (1) and at least one outer chamber (2) arranged after the inner chamber as seen for example in Figure 3.

[0030] Each chamber (1, 2) of the nozzle comprises at least one inlet opening connected to a fluid inlet duct and

a plurality of outlet openings through which the fluid leaves out the nozzle.

[0031] The key of the present invention is that the nozzle comprises at least one fluid distributor (3), such as the one seen in Figure 1, arranged in at least one of the chambers (1, 2) which is a hollow body intended for the flow of the fluid crossing said chamber (1, 2) in which it is found. In an exemplary embodiment, the fluid distributor (3) is removable and in another exemplary embodiment it is integrally shaped to fit the chamber of the nozzle

[0032] The fluid distributor (3) has a configuration corresponding to the geometry of the interior of the chamber (1, 2) and it is connected to a first opening that is an inlet opening for allowing the flow of the fluid therein and it comprises a plurality of second openings (4) aligned with the outlet openings of the chamber (1, 2) in order to allow the outlet of the flow through the outlet openings in a uniform manner. Figure 2 shows a fluid distributor (3) placed in the inner chamber of a nozzle.

[0033] The materials used for the production of the fluid distributor (3) are materials that are insoluble to the fluid crossing therethrough. Said materials could be porous or not. In the case where they are porous, said porosity depends on the viscosity of the fluid crossing therethrough in order to ensure the best distribution of the fluid towards all the outlet openings of the chamber. Figure 5 shows how the porous material allows distributing the fluid in a uniform manner through several outlets.

[0034] Preferably, the nozzle has a circular configuration and the outside diameter of the fluid distributor (3) coincides with the inner diameter of the chamber.

[0035] Preferably, the diameter of the second openings (4) of the fluid distributor is between 0.0001 mm and 100 mm. In an even more preferred embodiment, the diameter of the second openings (4) of the distributor is between 0.01 mm and 2 mm.

[0036] An example of production of a fluid distributor of a multi-outlet nozzle to be used for electrohydrodynamic processing is described below. In this specific example, the multi-outlet nozzle comprises 20 needles.

[0037] To produce the fluid distributor, it is started with a hollow body that is molded in order to give it the same shape as the chamber of the nozzle. In an exemplary embodiment as shown in Figure 2, the chamber of the nozzle is circular and the material of the hollow body can be Teflon (PTFE), for example, and the fluid distributor has a circular configuration with a 5.7 cm diameter, like the chamber of the nozzle in which the internal fluid is deposited and which, in this exemplary embodiment, is paraffin

[0038] As the nozzle has 20 needles, the fluid distributor has 20 openings, each having a 1 mm diameter in this case, and the distance between holes is 8 mm. These outlet openings are oriented towards the next chamber (in this case towards the external fluid chamber) and, on the opposite side, facing towards the opposite side, there is an opening, which preferably is larger and, in this case,

is 1.5 mm wide which is intended to allow the connection of the fluid distributor with a needle through which it is connected to the feeding system of the internal fluid.

[0039] In order to test the efficiency of the use of the nozzle, an encapsulation of paraffins in polyvinylpyrrolidone (PVP) was made through coaxial electrohydrodynamic processing. In this case, polyvinylpyrrolidone dissolved in ethanol was used as outer solution and liquid paraffin was used as the inner solution. The same process was carried out with one of the known nozzles from the state of the art and with the nozzle described in the present invention.

[0040] In the example, the electrospinning was carried out with the high-performance nozzle having 40 stainless steel needles arranged concentrically in order to carry out coaxial electrohydrodynamic processing. The conditions of the process in this example are: the flow rate of the inner solution 50 ml/h, the flow rate of the outer solution 60 ml/h, the distance between the nozzle and the collector 28 cm, the voltage of the nozzle 23 KV, the voltage of the collector 25 KV and the duration 3 hours. [0041] When a nozzle from the state of the art is used, the paraffin is not distributed uniformly over all the needles and leaves through a third of the outlets with different flow rates. This causes the encapsulation performance to be zero and that the block that is gathered in the collector has the appearance of a wet product (due to the lack of encapsulation of the paraffin). When using the nozzle of the present invention comprising a fluid distributor, a block with a high encapsulation performance (95%) is obtained.

[0042] Figure 4 shows an image of the morphology of polyvinylpyrrolidone and RT5 fibers obtained by coaxial electrohydrodynamic or aerohydrodynamic processing using a multi-outlet nozzle as described herein.

Claims

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- Multi-outlet nozzle for electrohydrodynamic or aerohydrodynamic processing operations and which is of the type comprising at least one chamber for the flow of a fluid with:
 - an inlet opening connected to a fluid inlet duct,
 a plurality of outlet openings through which the fluid leaves the nozzle,

and it is **characterized in that** it comprises a fluid distributor (3), arranged in the chamber, which is a hollow body intended for the flow of the fluid crossing said chamber, and having a configuration corresponding to the geometry of the interior of the chamber (1, 2) and is connected to a first opening that is an inlet opening for allowing the flow of the fluid therein and comprises a plurality of second openings (4) aligned with the outlet openings of the chamber (1, 2) for allowing the outlet of the flow crossing it,

through the outlet openings in a uniform manner.

- 2. The multi-outlet nozzle according to claim 1 characterized in that it comprises two or more chambers (1, 2) and comprises a fluid distributor (3) in at least one of the chambers.
- 3. The multi-outlet nozzle according to claim 1 characterized in that it has a circular configuration and the outside diameter of the fluid distributor (3) coincides with the inner diameter of the chamber.
- 4. The multi-outlet nozzle according to claim 1 characterized in that the diameter of the second outlet openings (4) of the fluid distributor is between 0.0001 mm and 100 mm.
- 5. The multi-outlet nozzle according to claim 4 characterized in that the diameter of the second outlet openings (4) is between 0.01 mm and 2 mm.
- **6.** The multi-outlet nozzle according to claim 1 **characterized in that** the fluid distributor (3) is made of a porous material.
- 7. The multi-outlet nozzle according to claim 1 characterized in that the fluid distributor (3) is removable.
- **8.** The multi-outlet nozzle according to claim 1 **characterized in that** the fluid distributor (3) is integrally formed in the chamber.

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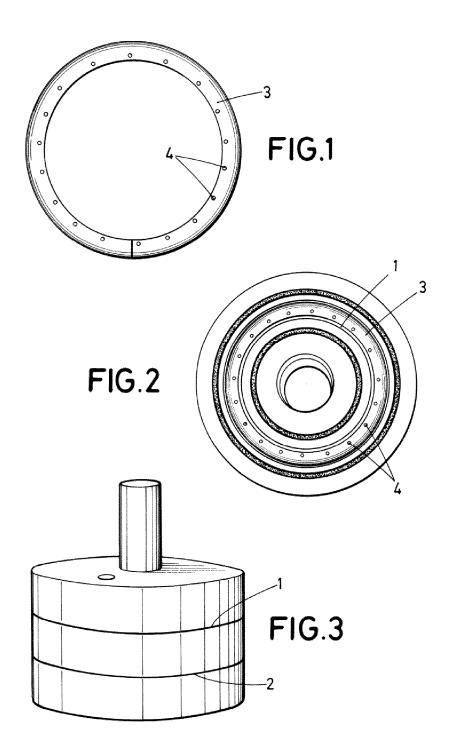
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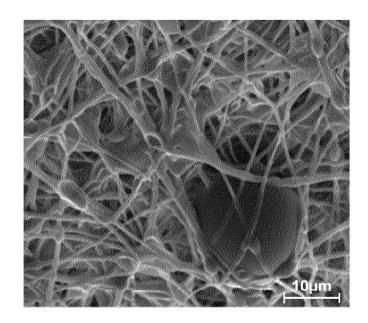
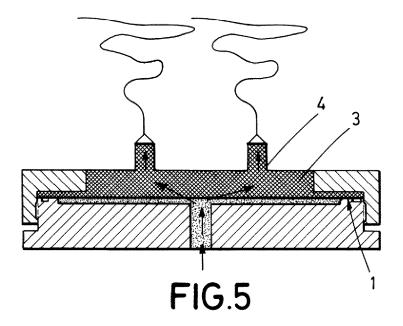


FIG.4



INTERNATIONAL SEARCH REPORT

International application No. PCT/ES2015/070845

5	A. CLASSIF	A. CLASSIFICATION OF SUBJECT MATTER						
	See extra sheet							
	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) B05B, D01D							
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	Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched							
15	Electronic da	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)						
	EPODOC, INVENES							
	C. DOCUMENTS CONSIDERED TO BE RELEVANT							
20	Category*	Citation of document, with indication, where appropri	ate, of the relevant passages	Relevant to claim No.				
25	X	WO 2006009854 A2 (UNIV YALE ET AL.) 2 page 4, lines 4 - 12; page 6, line 20 - page 7, lin lines 24 - 26; figure 1.	1-6, 8					
	A	CN 202809020U U (BOYIFEI EQUIPMENT I NEW MATERIALS) 20/03/2013, figure 2.	1-8					
30	A	US 2006081178 A1 (WILLEY ALAN D ET AL.) 20/04/2006, the whole document.		1-8				
	A	US 2012138701 A1 (OLIVIER MARC X ET 07/06/2012, the whole document.	1-8					
35								
	☐ Further d	ocuments are listed in the continuation of Box C.	☑ See patent family annex.					
40	* Special categories of cited documents: "T" later document published after the interprint document defining the general state of the art which is not considered to be of particular relevance. "E" earlier document but published on or after the international filing date "T" later document published after the interprint date and not in conflict with the to understand the principle or the invention of the principle or the principle or the principle or the invention of the principle or the principl		lict with the application but cited					
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55	Facsimile No	a: 91 349 53 04 A/210 (second sheet) (January 2015)	Telephone No. 91 3493023					

	INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/ES2015/070845	
5	Patent document cited in the search report	Publication date	Patent family member(s)	Publication date
	US2012138701 A1	07.06.2012	NONE	
10	US2006081178 A1	20.04.2006	JP2012050984 A WO2006044876 A1 US7160391 B2 JP2008516766 A EP1802401 A1	15.03.2012 27.04.2006 09.01.2007 22.05.2008 04.07.2007
15	CN202809020U U	20.03.2013	NONE	
	WO2006009854 A2	26.01.2006	NONE	
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55	Form PCT/ISA/210 (patent family annex) (January 2015)			

INTERNATIONAL SEARCH REPORT

International application No.

PCT/ES2015/070845 CLASSIFICATION OF SUBJECT MATTER **D01D1/09** (2006.01) **D01D4/06** (2006.01) **B05B1/14** (2006.01) **B05B5/025** (2006.01)

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

• US 2008131615 A [0012]