

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
2 November 2006 (02.11.2006)

PCT

(10) International Publication Number
WO 2006/116014 A2

(51) International Patent Classification:
B29C 47/86 (2006.01)

44313 (US). **SMITH, Daniel, J.** [US/US]; 2988 Ridgeline Trail, Stow, Ohio 44224 (US).

(21) International Application Number:
PCT/US2006/014977

(74) Agents: **MOXON, George, W.** et al.; Roetzel & Andress, LPA, 222 S. Main St., Akron, Ohio 44308 (US).

(22) International Filing Date: 21 April 2006 (21.04.2006)

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

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/673,729 21 April 2005 (21.04.2005) US

(71) Applicant (for all designated States except US): **THE UNIVERSITY OF AKRON** [US/US]; 302 Buchtel Common, Akron, Ohio 44325 (US).

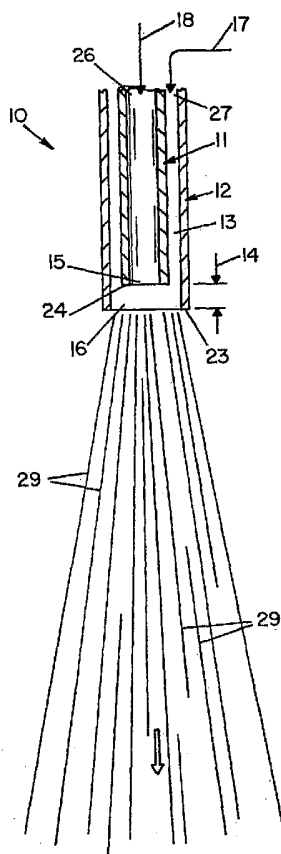
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,

(72) Inventors; and

(75) Inventors/Applicants (for US only): **RENEKER, Darrell, H.** [US/US]; 300 Hampshire Road, Akron, Ohio

[Continued on next page]

(54) Title: PROCESS FOR PRODUCING FIBERS AND THEIR USES



(57) Abstract: The present invention is directed to the use and production of fibers from one or more polymers or polymer composites. In one embodiment, the fibers of the present invention are nanofibers. In another embodiment, the fibers of the present invention are polymer nanofibers that further include at least one active agent or additive contained on, in, or about the polymer nanofibers of the present invention. In still another embodiment, the fibers of the present invention can be used to yield carbon and/or ceramic fibers/nanofibers.

WO 2006/116014 A2



FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT,
RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

— *without international search report and to be republished
upon receipt of that report*

PROCESS FOR PRODUCING FIBERS AND THEIR USES

FIELD OF THE INVENTION

The present invention is directed to the use and production of fibers from one
5 or more polymers or polymer composites. In one embodiment, the fibers of the
present invention are nanofibers. In another embodiment, the fibers of the present
invention are polymer nanofibers that further include at least one active agent or
additive contained on, in, or about the polymer nanofibers of the present invention.
In still another embodiment, the fibers of the present invention can be used to yield
10 carbon and/or ceramic fibers/nanofibers.

BACKGROUND OF THE INVENTION

The demand for nanofibers and nanofiber technology has grown in the past
few years. As a result, reliable sources for nanofibers, as well as economical
15 methods to produce nanofibers, have been sought. Uses for nanofibers will grow
with improved prospects for cost-efficient manufacturing, and the development of
and/or expansion of significant markets for nanofibers is almost certain in the next
few years. Currently, nanofibers are already being utilized in the high performance
filter industry. In the biomaterials area, there is a strong industrial interest in the
20 development of structures to support living cells (*i.e.*, scaffolds for tissue
engineering). The protective clothing and textile applications of nanofibers are of
interest to the designers of sports wear, and to the military, since the high surface
area per unit mass of nanofibers can provide a fairly comfortable garment with a
useful level of protection against chemical and biological warfare agents. Also of
25 interest is the use of nanofibers in the production of packaging, food preservation,
medical, agricultural, batteries and fuel cell applications, just to name a few.

Carbon nanofibers are potentially useful in reinforced composites, as supports
for catalysts in high temperature reactions, heat management, reinforcement of
elastomers, filters for liquids and gases, and as a component of protective clothing.
30 Nanofibers of carbon or polymer are likely to find applications in reinforced
composites, substrates for enzymes and catalysts, applying pesticides to plants,
textiles with improved comfort and protection, advanced filters for aerosols or

particles with nanometer scale dimensions, aerospace thermal management application, and sensors with fast response times to changes in temperature and chemical environment. Ceramic nanofibers made from polymeric intermediates are likely to be useful as catalyst supports, reinforcing fibers for use at high
5 temperatures, and for the construction of filters for hot, reactive gases and liquids.

Of interest is the ability to embed/sequester on, in, or about a nanofiber one or more therapeutic, active and/or chemical agents. Of particular interest is the use of therapeutic, active and/or chemical agents that are typically ignored due to their inability to survive the processing conditions necessary to produce a desired polymer
10 product. Accordingly, there is a need for a method or methods that would permit the production of fibers, even polymer fibers, while simultaneously allowing for the inclusion of, embedding in, and/or coating of the polymer fibers with one or more of a wide variety of therapeutic, active and/or chemical agents.

15 SUMMARY OF THE INVENTION

The present invention is directed to the use and production of fibers from one or more polymers or polymer composites. In one embodiment, the fibers of the present invention are nanofibers. In another embodiment, the fibers of the present invention are polymer nanofibers that further include at least one active agent or
20 additive contained on, in, or about the polymer nanofibers of the present invention. In still another embodiment, the fibers of the present invention can be used to yield carbon and/or ceramic fibers/nanofibers.

In one embodiment, the present invention relates to a method for forming nanofibers comprising the steps of: (i) feeding at least one fiber-forming material
25 and at least one additive into an annular column, the column having an exit orifice; (ii) directing the at least one fiber-forming material and at least one additive into an gas jet space, thereby forming an annular film of a combination of at least one fiber-forming material and at least one additive, the annular film having an inner circumference; and (iii) simultaneously forcing gas through a gas column, which is
30 concentrically positioned within the annular column, and into the gas jet space, thereby causing the gas to contact the inner circumference of the annular film, and ejects the combination of the at least one fiber-forming material and the at least one

additive from the exit orifice of the annular column in the form of a plurality of strands of fiber-forming material and additive that solidify and form nanofibers having a diameter up to about 25,000 nanometers.

In another embodiment, the present invention relates to a method for forming a plurality of nanofibers from a single nozzle comprising the steps of: (A) providing a nozzle, the nozzle comprising: a center tube; a first supply tube that is positioned concentrically around and apart from the center tube, wherein the center tube and the first supply tube form a first annular column, and wherein the center tube is positioned within the first supply tube so that a first gas jet space is created between a lower end of the center tube and a lower end of the supply tube; a middle gas tube positioned concentrically around and apart from the first supply tube, forming a second annular column; and a second supply tube positioned concentrically around and apart from the middle gas tube, wherein the middle gas tube and second supply tube form a third annular column, and wherein the middle gas tube is positioned within the second supply tube so that a second gas jet space is created between a lower end of the middle gas tube and a lower end of the second supply tube; (B) feeding at least one combination of at least one fiber-forming material and at least one additive into the first and second supply tubes; (C) directing the at least one combination of at least one fiber-forming material and at least one additive into the first and second gas jet spaces, thereby forming an annular film of the at least one fiber-forming material and the at least one additive in the first and second gas jet spaces, each annular film having an inner circumference; and (D) simultaneously forcing gas through the center tube and the middle gas tube, and into the first and second gas jet spaces, thereby causing the gas to contact the inner circumference of the annular films in the first and second gas jet spaces, and ejecting the at least one fiber-forming material and the at least one additive from the exit orifices of the first and third annular columns in the form of a plurality of strands of fiber-forming material and additive that solidify and form nanofibers having a diameter up to about 25,000 nanometers.

In still another embodiment, the present invention relates to a method for forming a plurality of nanofibers from a single nozzle comprising the steps of: (A) providing a nozzle, the nozzle comprising: a center tube; a first supply tube that is

positioned concentrically around and apart from the center tube, wherein the center tube and the first supply tube form a first annular column, and wherein the center tube is positioned within the first supply tube so that a first gas jet space is created between a lower end of the center tube and a lower end of the supply tube; a middle
5 gas tube positioned concentrically around and apart from the first supply tube, forming a second annular column; and a second supply tube positioned concentrically around and apart from the middle gas tube, wherein the middle gas tube and second supply tube form a third annular column, and wherein the middle gas tube is positioned within the second supply tube so that a second gas jet space
10 is created between a lower end of the middle gas tube and a lower end of the second supply tube; (B) feeding at least one fiber-forming material and at least one additive into the first and second supply tubes; (C) directing the at least one fiber-forming material and at least one additive into the first and second gas jet spaces, thereby forming an annular film of the at least one fiber-forming material and the at
15 least one additive in the first and second gas jet spaces, each annular film having an inner circumference; and (D) simultaneously forcing gas through the center tube and the middle gas tube, and into the first and second gas jet spaces, thereby causing the gas to contact the inner circumference of the annular films in the first and second gas jet spaces, and ejecting the at least one fiber-forming material and the at least
20 one additive from the exit orifices of the first and third annular columns in the form of a plurality of strands of fiber-forming material and additive that solidify and form nanofibers having a diameter up to about 25,000 nanometers.

BRIEF DESCRIPTION OF THE DRAWINGS

25 Figure 1 is a cross-section schematic diagram of an apparatus for producing nanofibers according to the present invention;

Figure 2 is a cross-sectional schematic diagram of another embodiment of an apparatus for producing nanofibers according to the present invention, wherein the apparatus includes a lip cleaner assembly;

30 Figure 3 is a cross-sectional schematic diagram of still another embodiment of an apparatus for producing nanofibers according to the present invention, wherein the apparatus includes an outer gas shroud assembly;

Figure 4 is a cross-sectional schematic diagram of yet another embodiment of an apparatus for producing nanofibers according to the present invention, wherein the apparatus includes an outer gas shroud, and the shroud is modified with a partition;

5 Figure 5 is a cross-sectional view taken along line 5–5 of the embodiment shown in Figure 3;

Figure 6 is a cross-sectional schematic diagram of one embodiment of an apparatus for producing nanofibers according to the present invention, wherein the apparatus is designed for batch processes;

10 Figure 7 is a cross-sectional schematic diagram of still another embodiment of an apparatus for producing nanofibers according to the present invention, wherein the apparatus is designed for continuous processes;

Figure 8 is a cross-sectional schematic diagram of still another embodiment of an apparatus for producing nanofibers according to the present invention, wherein
15 the apparatus is designed for the production of a mixture of nanofibers from one of more fiber-forming materials and/or one or more additives;

Figure 9 is a cross-sectional schematic diagram of still another embodiment of an apparatus for producing nanofibers according to the present invention, wherein the apparatus includes an outer gas shroud assembly; and

20 Figure 10 is a cross-sectional schematic diagram of still another embodiment of an apparatus for producing nanofibers according to the present invention, wherein the apparatus includes an outer gas shroud having a partition directed radially inward at an end thereof.

25 DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to the use and production of fibers from one or more polymers or polymer composites. In one embodiment, the fibers of the present invention are nanofibers. In another embodiment, the fibers of the present invention are polymer nanofibers that further include at least one active agent or
30 additive contained on, in, or about the polymer nanofibers of the present invention. In still another embodiment, the fibers of the present invention can be used to yield carbon and/or ceramic fibers/nanofibers.

As used herein nanofibers are fibers having an average diameter in the range of about 1 nanometer to about 25,000 nanometers (25 microns). In another embodiment, the nanofibers of the present invention are fibers having an average diameter in the range of about 1 nanometer to about 10,000 nanometers, or about 1
5 nanometer to about 5,000 nanometers, or about 3 nanometers to about 3,000 nanometers, or about 7 nanometers to about 1,000 nanometers, or even about 10 nanometers to about 500 nanometers. In another embodiment, the nanofibers of the present invention are fibers having an average diameter of less than 25,000 nanometers, or less than 10,000 nanometers, or even less than 5,000 nanometers.
10 In still another embodiment, the nanofibers of the present invention are fibers having an average diameter of less than 3,000 nanometers, or less than about 1,000 nanometers, or even less than about 500 nanometers. Additionally, it should be noted that here, as well as elsewhere in the text, ranges may be combined.

Various methods/techniques can be used to produce fibers, more particularly
15 nanofibers, in accordance with the present invention. Melt-blowing, Nanofibers by Gas Jet (NGJ) process, and electrospinning are included among these techniques. In a melt-blowing process, a stream of molten polymer or other fiber-forming material is typically extruded into a jet of gas to form fibers.

A technique and apparatus for forming fibers having a diameter of less than
20 3,000 nanometers according to the NGJ technique is described in United States Patent Nos. 6,382,526; 6,520,425; and 6,695,992, the disclosures of which are incorporated herein by reference in their entireties.

The electrospinning of liquids and/or solutions capable of forming fibers, also known within the fiber forming industry as electrostatic spinning, is well known and
25 has been described in a number of patents as well as in the general literature. The process of electrospinning generally involves the creation of an electrical field at the surface of a liquid. The resulting electrical forces create a jet of liquid that carries electrical charge. Thus, the liquid jets may be attracted to other electrically charged objects at a suitable electrical potential. As the jet of liquid elongates and travels, it
30 will harden and dry. The hardening and drying of the elongated jet of liquid may be caused by cooling of the liquid, *i.e.*, where the liquid is normally a solid at room temperature; evaporation of a solvent, *e.g.*, by dehydration, (physically induced

hardening); or by a curing mechanism (chemically induced hardening). The produced fibers are collected on a suitably located, oppositely charged receiver and subsequently removed from it as needed, or directly applied to an oppositely charged or grounded generalized target area.

5 Fibers produced by this process have been used in a wide variety of applications, and are known, from United States Patent Nos. 4,043,331; 4,878,908; and 6,753,454, all of which are incorporated herein by reference in their entireties. One of the major advantages of electrospun fibers is that very thin fibers can be produced having diameters, usually on the order of about 50 nanometers to about
10 25,000 nanometers (25 microns), or even on the order of about 50 nanometers to about 5,000 nanometers (5 microns). These fibers can be collected and formed into, for example, non-woven mats of any desired shape and thickness. It will be appreciated that, because of the very small diameter of the fibers, a mat or other product with very small interstices and high surface area per unit mass can be
15 produced.

Alternatively, nanofibers in accordance with the present invention can be formed by other techniques, as known in the art. Such techniques include, but are not limited to, phase separation, casting in pores, and slitting of a film. These techniques are discussed in PCT Publication No. WO 03/086234, which is
20 incorporated herein by reference in its entirety.

An exemplary method for producing the nanofibers of the present invention will be described in detail below. It should be noted that the present invention is not limited to the following production method. Rather, as is discussed above, a wide range of production methods can be utilized to produce nanofibers in accordance
25 with the present invention.

As mentioned above, nanofibers can be produced by using pressurized gas. This is generally accomplished by a process wherein the mechanical forces supplied by an expanding gas jet create nanofibers from a fluid that flows through a nozzle. This process may be referred to as Nanofibers by Gas Jet (NGJ). NGJ is a broadly
30 applicable process that produces nanofibers from any spinnable fluid or fiber-forming material.

In general, a spinnable fluid or fiber-forming material is any fluid or material that can be mechanically formed into a cylinder or other long shapes by stretching and then solidifying the liquid or material. This solidification can occur by, for example, cooling, chemical reaction, coalescence, or removal of a solvent.

5 Examples of spinnable fluids include molten pitch, polymer solutions, polymer melts, polymers that are precursors to ceramics, and molten glassy materials. Some preferred polymers include nylon, fluoropolymers, polyolefins, polyimides, polyesters, polycaprolactones, and other engineering polymers, or textile forming polymers. In another embodiment, the spinnable fluid or fiber-forming material can be any edible

10 material that can be mechanically formed into a cylinder or other long shapes by stretching and then solidifying the liquid or material. The terms spinnable fluid and fiber-forming material may be used interchangeably throughout this specification without any limitation as to the fluid or material being used. As those skilled in the art will appreciate, a variety of fluids or materials can be employed to make fibers

15 including pure liquids, solutions of fibers, mixtures with small particles and biological polymers.

An example of a nozzle 10 that can be utilized to produce fibers and/or employed in a process in accordance with the present invention is described with reference to Figure 1. Nozzle 10 includes a center tube 11 having an entrance

20 orifice 26 and an outlet orifice 15. The diameter of center tube 11 can vary based upon the need for gas flow, which impacts the velocity of the gas as it moves a film of liquid across the jet space 14, as will be described below. In one embodiment, the diameter of tube 11 is from about 0.5 to about 10 mm, or even from about 1 to about 2 mm. Likewise, the length of tube 11 can vary depending upon construction

25 conveniences, heat flow considerations, and shear flow in the fluid. In a one embodiment, the length of tube 11 will be from about 1 to about 20 cm, or even from about 2 to about 5 cm. Positioned concentrically around and apart from the center tube 11 is a supply tube 12, which has an entrance orifice 27 and an outlet orifice 16. Center tube 11 and supply tube 12 create an annular space or column 13. This

30 annular space or column 13 has a width, which is the difference between the inner and outer diameter of the annulus, that can vary based upon the viscosity of the fluid and the maintenance of a suitable thickness of fiber-forming material fluid on the

inside wall of gas jet space 14. In one embodiment, the width is from about 0.05 to about 5 mm, or even from about 0.1 to about 1 mm. Center tube 11 is vertically positioned within supply tube 12 so that a gas jet space 14 is created between lower end 24 of center tube 11 and lower end 23 of supply tube 12. The position of center tube 11 is adjustable relative to lower end 23 of supply tube 12 so that the length of gas jet space 14 is adjustable. Gas jet space 14, *i.e.*, the distance between lower end 23 and lower end 24, is adjustable so as to achieve a controlled flow of fluid along the inside of tube 12, and optimal conditions for nanofiber production at the end 23 of tube 12. In one embodiment, this distance is from about 0.1 to about 10 mm, or even from about 1 to about 2 mm. It should be understood that gravity will not impact the operation of this apparatus for producing fibers in accordance with the present invention, but for purposes of explaining the present invention, reference will be made to the apparatus as it is vertically positioned as shown in the figures.

It should be appreciated that the supply tube outlet orifice 16 and gas jet space 14 can have a number of different shapes and patterns. For example, the space 14 can be shaped as a cone, bell, trumpet, or other shapes to influence the uniformity of fibers launched at the orifice. The shape of the outlet orifice 16 can be circular, elliptical, scalloped, corrugated, or fluted. Still further, the inner wall of supply tube 12 can include slits or other manipulations that may alter fiber formation. These shapes influence the production rate and the distribution of fiber diameters in various ways.

According to the present invention, nanofibers are produced by using the apparatus of Figure 1 by the following method. Fiber-forming material is provided by a source 17, and fed through annular space 13. The fiber-forming material is directed into gas jet space 14. Simultaneously, pressurized gas is forced from a gas source 18 through the center tube 11 and into the gas jet space 14.

Within gas jet space 14 it is believed that the fiber-forming material is in the form of an annular film. In other words, fiber-forming material exiting from the annular space 13 into the gas jet space 14 forms a thin layer of fiber-forming material on the inside wall of supply tube 12 within gas jet space 14. This layer of fiber-forming material is subjected to shearing deformation by the gas jet exiting from center tube outlet orifice 15 until it reaches the fiber-forming material supply tube

outlet orifice 16. At this point, it is believed that the layer of fiber-forming material is blown apart into many small strands 29 by the expanding gas and ejected from orifice 16 as shown in Figure 1. Once ejected from orifice 16, these strands solidify and form nanofibers. This solidification can occur by cooling, chemical reaction,
5 coalescence, ionizing radiation or removal of solvent.

As noted above, the fibers produced according to this process can be, in some embodiments, nanofibers. Nanofibers according to the present invention are defined as discussed above. In another embodiment, nanofibers according to the present invention are those fibers that have an average diameter that is less than
10 about 25,000 nanometers, less than about 10,000 nanometers, less than about 5,000 nanometers, less than about 3,000 nanometers, or less than about 1,000 nanometers, or even less than about 500 nanometers. Those of skill in the art will recognize how to modify the above-mentioned process and apparatus to yield nanofibers having a desired average diameter selected from the average diameters
15 listed above.

The diameter of fibers formed in accordance with the present invention can be adjusted by controlling various conditions including, but not limited to, temperature and gas pressure. The length of these fibers can vary widely to include fibers that are as short as about 0.0001 mm up to those fibers that are about many km in
20 length. Within this range, the fibers can have a length from about 1 mm to about 1 km, or even from about 1 cm to about 1 mm. The length of these fibers can be adjusted by controlling the solidification rate.

As discussed above, pressurized gas is forced through center tube 11 and into jet space 14. This gas should be forced through center tube 11 at a sufficiently
25 high pressure so as to carry the fiber-forming material along the wall of jet space 14 and create nanofibers. Therefore, in one embodiment, the gas is forced through center tube 11 under a pressure of from about 10 to about 5,000 pounds per square inch (psi), or even from about 50 to about 500 psi.

The term gas as used throughout this specification, includes any gas. Non-
30 reactive gases are preferred and refer to those gases, or combinations thereof, that will not deleteriously impact the fiber-forming material. Examples of these gases include, but are not limited to, nitrogen, helium, argon, air, nitrogen, helium, argon,

air, carbon dioxide, steam, fluorocarbons, fluorochlorocarbons, and mixtures thereof. It should be understood that for purposes of this specification, gases will refer to those super heated liquids that evaporate at the nozzle when pressure is released, e.g., steam. It should further be appreciated that these gases can or may contain
5 solvent vapors that serve to control the rate of drying of the nanofibers made from polymer solutions. Still further, useful gases include those that react in a desirable way, including mixtures of gases and vapors or other materials that react in a desirable way. For example, it may be useful to employ oxygen to stabilize the production of nanofibers from pitch. Also, it may be useful to employ gas streams
10 that include molecules that serve to crosslink polymers. Still further, it may be useful to employ gas streams that include metals that serve to improve the production of ceramics.

In another embodiment, shown in Figure 2, nozzle 10 further comprises a lip cleaner 30. Within this assembly, an outer gas tube 19 is positioned concentrically
15 around and apart from supply tube 12. Outer gas tube 19 extends along supply tube 12 and thereby creates a gas annular column 21. Lower end 22 of outer gas tube 19 and lower end 23 of supply tube 12 form lip cleaner orifice 20. In one embodiment, lower end 22 and lower end 23 are on the same horizontal plane (flush) as shown in Figure 2. In another embodiment, however, lower ends 22 and 23 may be on
20 different horizontal planes as shown in Figures 3 and 4.

As also shown in Figure 2 outer gas tube 19 tapers and thereby reduces the size of annular space 21. Pressurized gas is forced through outer gas tube 19 and exits from outer gas tube 19 at lip cleaner orifice 20, thereby preventing the build up of residual amounts of fiber-forming material that can accumulate at lower end 23 of
25 supply tube 12. The gas that is forced through gas annular column 21 should be at a sufficiently high pressure so as to prevent accumulation of excess fiber-forming material at lower end 23 of supply tube 12, yet should not be so high that it disrupts the formation of fibers. Therefore, in one embodiment, the gas is forced through the gas annular column 21 under a pressure of from about 0 to about 1,000 psi, or even
30 from about 10 to about 100 psi. The gas flow through lip cleaner orifice 20 also affects the exit angle of the strands of fiber-forming material exiting from outlet orifice

15, and therefore lip cleaner 30 of this environment serves both to clean the lip and control the flow of exiting fiber strands.

In yet another embodiment, which is shown in Figures 3, 4, and 5, a shroud gas tube 31 is positioned concentrically around outer gas tube 19. Pressurized gas
5 at a controlled temperature is forced through shroud gas tube 31 so that it exits from the shroud gas tube orifice 32 and thereby creates a moving shroud of gas around the nanofibers. This shroud of gas controls the cooling rate, solvent evaporation rate of the fluid, or the rate chemical reactions occurring within the fluid. It should be understood that the general shape of the gas shroud is controlled by the width of the
10 annular tube orifice 32 and its vertical position with respect to bottom 23 of tube 12. The shape is further controlled by the pressure and volume of gas flowing through the shroud. It should be further understood that the gas flowing through the shroud is preferably under a relatively low pressure and at a relatively high volume flow rate in comparison with the gas flowing through center tube 11.

15 In one embodiment, shroud gas tube orifice 32 is in an open configuration, as shown in Figure 3. In another embodiment, as shown in Figure 4, orifice 32 is in a constricted configuration, wherein the orifice is partially closed by a shroud partition 33 that adjustably extends from shroud gas tube 31 toward lower end 23.

In practicing the present invention, spinnable fluid or fiber-forming material
20 can be delivered to annular space 13 by several techniques. For example, and as shown in Figure 6, the fiber-forming material can be stored within nozzle 10. This is especially useful for batch operations. As with the previous embodiments, nozzle 10 will include a center tube 11. Positioned, preferably concentrically, around center tube 11 is a fiber-forming material container 34, comprising container walls 38, and
25 defining a storage space 35. The size of storage space 35, and therefore the volume of spinnable fluid stored within it, will vary according to the particular application to which the present invention is put. Fiber-forming material container 34 further comprises a supply tube 12. Center tube 11 is inserted into fiber-forming material container 34 in such a way that a center tube outlet orifice 15 is positioned
30 within the outlet tube 37, creating a gas jet space 14 between the lower end 24 of center outlet 11 and the lower end 36 of outlet tube 37. The position of center tube 11 is vertically adjustable relative to lower end 36 so that the length of the gas jet

space 14 is likewise adjustable. As with previously described embodiments, gas jet space 14, *i.e.*, the distance between lower end 36 and lower end 24, is adjustable so as to achieve a uniform film within space 14 and thereby produce uniform fibers with small diameters and high productivity. In one embodiment, this distance is from
5 about 1 to about 2 mm, or even from about 0.1 to about 5 mm. The length of outlet tube 37 can be varied according to the particular application of the present invention. If container wall 38 is of sufficient thickness, such that a suitable gas jet space can be created within wall 38, then outlet tube 37 may be eliminated.

According to this embodiment, nanofibers are produced by using the
10 apparatus of Figure 6 according to the following method. Pressure is applied to the container so that fiber-forming material is forced from storage space 35 into gas jet space 14. The pressure that is applied can result from gas pressure, pressurized fluid, or molten polymer from an extruder. Simultaneously, pressurized gas is forced from a gas source 18, through center tube 11, and exits through center tube orifice
15 15 into gas jet space 14. As with the previous embodiments, heat may be applied to the fiber-forming material prior to or after being placed in fiber-forming material container 34, to the pressurized gas entering center tube 11, and/or to storage space 35 by heat source 39 or additional heat sources. Fiber-forming material exiting from storage space 35 into gas jet space 14 forms a thin layer of fiber-forming material on
20 the inside wall of gas jet space 14. This layer of fiber-forming material is subjected to shearing deformation, or other modes of deformation such as surface wave, by the gas jet until it reaches container outlet orifice 36. There the layer of fiber-forming material is blown apart, into many small strands, by the expanding gas.

In still another embodiment, as shown in Figure 7, the fiber-forming material
25 can be delivered on a continuous basis rather than a batch basis as in Figure 6. In this embodiment, the apparatus is a continuous flow nozzle 41. Consistent with previous embodiments, nozzle 41 comprises a center tube 11, a supply tube 12, an outer gas tube 19, and a gas shroud tube 31. Supply tube 12 is positioned concentrically around center tube 11. Outer gas tube 19 is positioned concentrically around supply tube 12. Gas shroud tube 31 is positioned concentrically around
30 outer gas tube 19. Center tube 11 has an entrance orifice 26 and an outlet orifice 15. As in previous embodiments, the diameter of center tube 11 can vary. In one

embodiment, the diameter of tube 11 is from about 1 to about 20 mm, or even from about 2 to about 5 mm. Likewise the length of tube 11 can vary. In one embodiment, the length of tube 11 will be from about 1 to about 10 cm, or even from about 2 to about 3 cm.

5 Positioned concentrically around the center tube 11 is a supply tube 12 that has an entrance orifice 27 and an outlet orifice 16. The center tube 11 and supply tube 12 create an annular space or column 13. This annular space or column 13 has a width, which is the difference between the inner and outer diameter of the annulus. As would be evident from the attached Figures, this width can vary. In
10 one embodiment, the width is from about 0.05 to about 5 mm, or even from about 0.1 to about 1 mm.

Center tube 11 is vertically positioned within the supply tube 12 so that an gas jet space 14 is created between the lower end 24 of center tube 11 and the lower end 23 of supply tube 12. The position of center tube 11 is adjustable relative to
15 supply tube outlet orifice 16 so that the size of gas jet space 14 is adjustable. As with previously embodiments, the gas jet space 14, *i.e.*, the distance between lower end 23 and lower end 24, is adjustable. In one embodiment this distance is from about 0.1 to about 10 mm, or even from about 1 to about 2 mm.

Center tube 11 is attached to an adjustment device 42 that can be
20 manipulated such as by mechanical manipulation. In one particular embodiment as shown in Figure 7, the adjustment device 42 is a threaded rod that is inserted through a mounting device 43 and is secured thereby by a pair of nuts threaded onto the rod.

In this embodiment, supply tube 12 is in fluid tight communication with supply
25 inlet tube 51. Center tube 11 is in fluid tight communication with pressurized gas inlet tube 52, outer gas tube 19 is in fluid tight communication with the lip cleaner gas inlet tube 53, and gas shroud tube 31 is in fluid tight communication with shroud gas inlet tube 54. This fluid tight communication is achieved by use of a connector, but other means of making a fluid tight communication can be used, as known by those
30 skilled in the art.

According to the present invention, nanofibers are produced by using the apparatus of Figure 7 by the following method. Fiber-forming material is provided by a source 17 through supply inlet tube 51 into and through annular space 13, and then into gas jet space 14. In one embodiment, the fiber-forming material is supplied
5 to the supply inlet tube 51 under a pressure of from about 0 to about 15,000 psi, or even from about 100 to about 1,000 psi. Simultaneously, pressurized gas is forced through inlet tube 52, through center tube 11, and into gas jet space 14. As with previously described embodiments, it is believed that fiber-forming material is in the form of an annular film within gas jet space 14. This layer of fiber-forming material is
10 subjected to shearing deformation by the gas jet exiting from the center tube outlet orifice 15 until it reaches the fiber-forming material supply tube outlet orifice 16. At this point, it is believed that the layer of fiber-forming material is blown apart into many small strands by the expanding gas. Once ejected from orifice 16, these strands solidify in the form of nanofibers. This solidification can occur by cooling,
15 chemical reaction, coalescence, ionizing radiation or removal of solvent. As with previously described embodiments also simultaneously, pressurized gas is supplied by gas source 25 to lip cleaner inlet tube 53 into outer gas tube 19.

As with previous embodiments, the outer gas tube 19 extends along supply tube 12 and thereby creates an annular column of gas 21. The lower end 22 of gas
20 annular column 21 and the lower end 23 of supply tube 12 form a lip cleaner orifice 20. In this embodiment, lower end 22 and lower end 23 are on the same horizontal plane (flush) as shown in Figure 7. As noted above, however, lower ends 22 and 23 may be on different horizontal planes. The pressurized gas exiting through lip cleaner orifice 20 prevents the buildup of residual amounts of fiber-forming material
25 that can accumulate at lower end 23 of supply tube 12. Simultaneously, pressurized gas is supplied by gas source 28 through shroud gas inlet tube 54 to shroud gas tube 31. Pressurized gas is forced through the shroud gas tube 31 and it exits from the shroud gas tube orifice 32 thereby creating a shroud of gas around the nanofibers that control the cooling rate of the nanofibers exiting from tube orifice 16.
30 In one particular embodiment, fiber-forming material is supplied by an extruder.

A mixture of nanofibers can be produced from the nozzles shown in Figures 8 through 10. In these embodiments, a plurality of gas tubes and supply tubes are concentrically positioned in an alternating manner such that a plurality of gas jet spaces are created.

5 As shown in Figure 8, nozzle 60 includes a center tube 11 having an entrance orifice 26 and an outlet orifice 15. The diameter of center tube 11 can vary based upon the need for gas flow. Center tube 11 may be specifically adapted to carry a pressurized gas. Positioned concentrically around center tube 11 is a first supply tube 61 that has an entrance orifice 63 and an exit orifice 65. Center tube 11 and
10 first supply tube 61 create a first supply annular space or column 69. First supply tube 61 may be specifically adapted to carry a fiber-forming material. Furthermore, center tube 11 and first supply tube 61 may be positioned such that they are essentially parallel to each other.

 As with the embodiments described above, center tube 11 is positioned within
15 first supply tube 61 so that a first gas jet space 71 is created between the lower end 24 of center tube 11 and the lower end 67 of first supply tube 61. The position of center tube 11 may be adjustable relative to lower end 67 of first supply tube 61 so that the length of first gas jet space 71 is adjustable. Also, the width of first supply annular space or column 69 can be varied to accommodate the viscosity of the fluid
20 and the maintenance of a suitable thickness of fiber-forming material on the inside wall of first gas jet space 71.

 Nozzle 60 also has a middle gas tube 73 positioned concentrically around and apart from first supply tube 61. Middle gas tube 73 extends along first supply tube 61 and thereby creates a middle gas annular column 75. Middle gas tube 73 has an
25 entrance orifice 81 and an exit orifice 83.

 Unlike the embodiments described above, a second supply tube 77 is positioned concentrically around middle gas tube 73, which creates a second supply annular space or column 79. Second supply tube 77 has an entrance orifice 85 and an exit orifice 87. As with first supply tube 61, second supply tube 77 may be
30 specifically adapted to carry a fiber-forming material. Middle gas tube 73 is positioned within second supply tube 77 so that a second gas jet space 92 is created between the lower end 88 of middle gas tube 73 and the lower end 90 of second

supply tube 77. The position of middle gas tube 73 may be adjustable relative to lower end 90 of second supply tube 77 so that the length of second gas jet space 92 is adjustable. The dimensions of first and second gas jet spaces, 71 and 92 respectively, are adjustable in order to achieve a controlled flow of fiber-forming material along the inside of first supply tube 61 and second supply tube 77, and thereby provide optimal conditions for nanofiber production at ends 67 and 90 of tubes 61 and 77. In one embodiment, the distance between ends 88 and 90, and between ends 24 and 67, is from about 0.1 to about 10 mm, or even from about 1 to about 2 mm. In one example of this embodiment, lower end 90 and lower end 67 are on different horizontal planes as shown in Figure 8. In another example of this embodiment, lower end 90 is on the same horizontal plane (flush) as lower end 67 (not shown).

For purposes of clarity, the embodiments as shown in Figures 8 through 10 feature two supply tubes and corresponding gas supply tubes, but it is envisioned that any multiple of supply tubes and gas tubes can be positioned concentrically around center tube 11 in the same repeating pattern as described above.

Nozzle 60 optionally further comprises a lip cleaner 30, as shown in Figure 8. Lip cleaner 30 comprises an outer air tube 19 positioned concentrically around and apart from second supply tube 77, as shown in Figure 8, or concentrically around the outermost supply tube if more than two supply tubes are present as mentioned above. Outer gas tube 19 extends along second supply tube 77 and thereby creates a gas annular column 21. A lower end 22 of outer gas tube 19 and lower end 90 of second supply tube 77 form lip cleaner orifice 20. As in the embodiments described above, lower ends 22 and 90 may also be on different horizontal planes as shown in Figure 8, or lower end 22 may be on the same horizontal plane (flush) as lower end 90 as shown in Figure 9. As shown in Figures 8 through 10, outer gas tube 19 can, in one embodiment, taper and thereby reduces the size of annular space 21 at lower end 22.

Nanofibers are produced by using the apparatus of Figure 8 by the following method. A first fiber-forming material is provided by a first material source 94, and fed through first annular space 69 and directed into first gas jet space 71. Pressurized gas is forced from a gas source through the center tube 11 and into first

gas jet space 71. This gas should be forced through center tube 11 at a sufficiently high pressure so as to carry the fiber-forming material along the wall of jet space 71 and create nanofibers, as mentioned in previous embodiments. A second fiber-forming material may be provided by the first material source (not shown) or by a second material source 96, and fed through second supply annular space 79. The second fiber-forming material is directed into second gas jet space 92. Pressurized gas is forced from a source through middle gas annular column 75 and into second gas jet space 92. This gas should be forced through middle gas annular column 75 at a sufficiently high pressure so as to carry the fiber-forming material along the wall of jet space 92 and create nanofibers, as mentioned in previous embodiments. Therefore, in one embodiment, the gas is forced through center tube 11 and middle gas tube 73 under a pressure of from about 10 to about 5,000 psi, or even from about 50 to about 500 psi.

Pressurized gas is also forced through outer gas tube 19 and exits from outer gas tube 19 at lip cleaner orifice 20, thereby preventing the build up of residual amounts of fiber-forming material that can accumulate at lower end 90 of supply tube 77. The gas flow through lip cleaner orifice 20 also affects the exit angle of the strands of fiber-forming material exiting from exit orifice 87, and therefore lip cleaner 30 of this environment serves both to clean the lip and control the flow of exiting fiber strands. In a similar manner, the gas exiting second supply tube exit orifice 87 also serves to clean lower end 67 of first supply tube 61 and controls the flow of fiber strands exiting from first supply tube 61. In this way, each gas tube functions as a lip cleaner for the supply tube that is concentrically interior to it.

The gas that is forced through gas annular column 21 should be at a sufficiently high pressure so as to prevent accumulation of excess fiber-forming material at lower end 90 of second supply tube 77, yet should not be so high that it disrupts the formation of fibers. Therefore, in one embodiment, the gas is forced through the gas annular column 21 under a pressure of from about 0 to about 1,000 psi, or even from about 10 to about 100 psi. The gas flow through lip cleaner orifice 20 also affects the exit angle of the strands of fiber-forming material exiting from outlet orifice 15, and therefore lip cleaner 30 of this environment serves both to clean the lip and control the flow of exiting fiber strands.

In other similar embodiments, which are shown in Figures 9 and 10, a shroud gas tube 31 is positioned concentrically around outer gas tube 19. Pressurized gas at a controlled temperature is forced through shroud gas tube 31 so that it exits from the shroud gas tube orifice 32 and thereby creates a moving shroud of gas around the nanofibers. This shroud of gas can control the solidification rate of the fiber-forming material by, for example influencing the cooling rate of a molten fiber-forming material, the solvent evaporation rate of the fiber-forming material, or the rate of chemical reactions occurring within the fiber-forming material. It should be understood that the general shape of the gas shroud is controlled by the width of the annular tube orifice 32 and its vertical position with respect to lower end 22 of outer gas tube 19. The shape is further controlled by the pressure and volume of gas flowing through the shroud. It should be further understood that the gas flowing through the shroud is generally under a relatively low pressure and at a relatively high volume flow rate in comparison with the gases flowing through center tube 11 and middle gas tube 73.

In one embodiment, shroud gas tube orifice 32 is in an open configuration, as shown in Figure 9. In another embodiment, as shown in Figure 10, orifice 32 is in a constricted configuration, wherein the orifice is partially closed by a shroud partition 33 that may adjustably extend radially inward from shroud gas tube 31 toward lower end 23.

It should be understood that there are many conditions and parameters that will impact the formation of fibers according to the present invention. For example, the pressure of the gas moving through any of the columns of the apparatus of this invention may need to be manipulated based on the fiber-forming material that is employed. Also, the fiber-forming material being used or the desired characteristics of the resulting nanofiber may require that the fiber-forming material itself or the various gas streams be heated. For example, the length of the nanofibers can be adjusted by varying the temperature of the shroud air. Where the shroud air is cooler, thereby causing the strands of fiber-forming material to quickly freeze or solidify, longer nanofibers can be produced. On the other hand, where the shroud air is hotter, and thereby inhibits solidification of the strands of fiber-forming material, the resulting nanofibers will be shorter in length. It should also be appreciated that

the temperature of the pressurized gas flowing through center tube 11 and middle gas tube 73 can likewise be manipulated to achieve or assist in these results. For example, acicular nanofibers of mesophase pitch can be produced where the shroud air is maintained at about 350°C. This temperature should be carefully controlled so that it is hot enough to cause the strands of mesophase pitch to be soft enough and thereby stretch and neck into short segments, but not too hot to cause the strands to collapse into droplets. In one embodiment, acicular nanofibers have lengths in the range of about 1,000 to about 2,000 nanometers.

Those skilled in the art will be able to heat the various gas flows using techniques that are conventional in the art. Likewise, the fiber-forming material can be heated by using techniques well known in the art. For example, heat may be applied to the fiber-forming material entering the supply tube, to the pressurized gas entering the center tube, or to the supply tube itself by a heat source 39, as shown in Figure 3 and 6, for example. In one particular embodiment, as shown in Figure 6, heat source 39 can include coils that are heated by a source 59.

In one embodiment of the present invention, carbon nanofiber precursors can be produced. Specifically, nanofibers of polymer, such as polyacrylonitrile, are spun and collected by using the process and apparatus of this invention. These polyacrylonitrile fibers are heated in air to a temperature of about 200 to about 400°C under tension to stabilize them for treatment at higher temperature. These stabilized fibers are then converted to carbon fibers by heating to approximately 1700°C under inert gas. In this carbonization process, all chemical groups, such as HCN, NH₃, CO₂, N₂ and hydrocarbons, are removed. After carbonization, the fibers are heated to temperatures in the range of about 2000°C to about 3000°C under tension. This process, called graphitization, makes carbon fibers with aligned graphite crystallites.

In another embodiment, carbon nanofiber precursors are produced by using mesophase pitch. These pitch fibers can then be stabilized by heating in air to prevent melting or fusing during high temperature treatment, which is required to obtain high strength and high modulus carbon fibers. Carbonization of the stabilized fibers is carried out at temperatures between 1000°C and 1700°C depending on the desired properties of the carbon fibers.

In another embodiment, NGJ is combined with electrospinning techniques. In these combined process, NGJ improves the production rate while the electric field maintains the optimal tension in the jet to produce orientation and avoid the appearance of beads on the fibers. The electric field also provides a way to direct
5 the nanofibers along a desired trajectory through processing machinery, heating ovens, or to a particular position on a collector. Electrical charge on the fiber can also produce looped and coiled nanofibers that can increase the bulk of the non-woven fabric made from these nanofibers.

Nanofibers can be combined into twisted yarns with an gas vortex, or even
10 more complicated woven, braided, knotted, or composite arrangements. Also, metal containing polymers can be spun into nanofibers and converted to ceramic nanofibers. This is a well known route to the production of high quality ceramics. The sol-gel process utilizes similar chemistry, but here linear polymers would be synthesized and therefore gels would be avoided. In some applications, a wide
15 range of diameters would be useful. For example, in a sample of fibers with mixed diameters, the volume-filling factor can be higher because the smaller fibers can pack into the interstices between the larger fibers.

Blends of nanofibers and textile size fibers may have properties that would, for example, allow a durable non-woven fabric to be spun directly onto a person,
20 such as a soldier or environmental worker, to create protective clothing that could absorb, deactivate, or create a barrier to chemical and biological agents.

It should also be appreciated that the average diameter and the range of diameters is affected by adjusting the gas temperature, the flow rate of the gas stream, the temperature of the fluid, and the flow rate of fluid. The flow of the fluid
25 can be controlled by a valve arrangement, by an extruder, or by separate control of the pressure in the container and in the center tube, depending on the particular apparatus used.

It should thus be evident that the NGJ methods and apparatus disclosed herein are capable of providing nanofibers by creating a thin layer of fiber-forming
30 material on the inside of an outlet tube, and this layer is subjected to shearing deformation until it reaches the outlet orifice of the tube. There, the layer of fiber-forming material is blown apart, into many small jets, by the expanding gas. No

apparatus has ever been used to make nanofibers by using pressurized gas. Further, the NGJ process creates fibers from spinnable fluids, such as mesophase pitch, that can be converted into high strength, high modulus, high thermal conductivity graphite fibers. It can also produce nanofibers from a solution or melt.

5 It may also lead to an improved nozzle for production of small droplets of liquids. It should also be evident that NGJ produces nanofibers at a high production rate. NGJ can be used alone or in combination with either or both melt blowing or electrospinning to produce useful mixtures of fiber geometries, diameters and lengths. Also, NGJ can be used in conjunction with an electric field, but it should be
10 appreciated that an electric field is not required.

In another embodiment, a polymer solution can be combined with a therapeutic substance to produce nanofibers that contain, sequester, and/or are coated with one or more desired therapeutic substance. Nanofibers containing one or more therapeutic substances can be used to form a variety of articles for use in
15 various medicals fields including, but not limited to, wound dressings, bandages, and cell scaffolds for tissue engineering. Alternatively, the therapeutic agent can be replaced by any chemical, active agent or additive such as one or more pesticides, fungicides, anti-bacterials, fertilizers, vitamins, hormones, chemical and/or biological indicators, protein, growth factors, growth inhibitors, antioxidants, dyes, colorants,
20 sweeteners, flavoring compounds, deodorants, etc. Products formed from nanofibers of the present invention that contain one or more additives, therapeutic and/or active agents enable delivery of such additives, therapeutic and/or active agents via their inclusion in, on or about the present invention's nanofibers. Possible delivery routes include, but are not limited to, dissolution, biodegradability, and
25 diffusion.

In one instance, nanofibers of the present invention can contain in, on or about the fibers a nitric oxide-releasing compound (NO-releasing compounds). Such NO-releasing compounds are known in the art, and are discussed in, for example, United States Patent No. 5,519,020, which is incorporated herein by reference in its
30 entirety. As is known in the art NO is a vital biological molecule. NO plays a central role in such diverse processes as host defense, cardiovascular regulation, signal transduction, neurotransmission and wound healing. The enzyme nitric oxide

synthase (NOS) converts L-arginine into L-citrulline and NO, and numerous cells involved in the wound healing process have shown NOS activity. The exact functions of NO in tissue repair have not been established, although a likely major role of NO is that of a cytotoxic or cytostatic agent released by macrophages and
5 other phagocytic cells during the early inflammatory phase. NO released from wound resident cells may also be important in unique cell signaling pathways and the re-establishment of the microcirculation as newly vascularized tissue is formed.

In another instance, the present invention also contemplates the inclusion of any substance in the form of molecules, particles, coatings, separated phases, gel
10 particles, small gas bubbles, liquid droplets and the like, that can be sequestered on, in or about the nanofibers of the present invention. As discussed above, one method for producing nanofibers that contain one or more active agents and/or additives on, in, or about the nanofibers is by the NGJ process. This method is particularly suited to the production of such nanofibers when the at least one active agent and/or
15 additive is soluble or can be dispersed in the polymer solution from which the nanofibers are to be formed.

Although the present invention is not limited thereto, the NGJ process is suitable for incorporation of therapeutic and/or active substances into the fibers, since this process can operate at room temperature, or at even lower temperatures,
20 which can be achieved by solvent evaporation during the formation of the fibers, or, by refrigeration of the gases in which the NGJ process is operated. This is especially useful for therapeutic, active and/or chemical substances that are degraded by exposure to high temperatures that are commonly encountered in conventional melt blowing, or in melt blowing processes which are optimized for
25 production of thin fibers. Additionally, NGJ permits the formation of nanofibers having smaller distribution of average fiber diameters. Thus, the formation of nanofibers is possible with increased quality control.

In another embodiment, upon leaving the NGJ process the nanofibers can be electrically charged by contact charging, or by the attachment of ions created in the
30 surrounding gas. This electrification may be useful in "fluffing" a non-woven fabric, or in collecting the fibers into a patterned structure, or for increasing their effectiveness in some filtration applications.

Although the invention has been described in detail with particular reference to certain embodiments detailed herein, other embodiments can achieve the same results. Variations and modifications of the present invention will be obvious to those skilled in the art and the present invention is intended to cover in the appended
5 claims all such modifications and equivalents.

CLAIMS

What is claimed is:

1. A method for forming nanofibers comprising the steps of:
 - (i) feeding at least one fiber-forming material and at least one additive into an annular column, the column having an exit orifice;
 - (ii) directing the at least one fiber-forming material and at least one additive into an gas jet space, thereby forming an annular film of a combination of at least one fiber-forming material and at least one additive, the annular film having an inner circumference; and
 - (iii) simultaneously forcing gas through a gas column, which is concentrically positioned within the annular column, and into the gas jet space, thereby causing the gas to contact the inner circumference of the annular film, and ejects the combination of the at least one fiber-forming material and the at least one additive from the exit orifice of the annular column in the form of a plurality of strands of fiber-forming material and additive that solidify and form nanofibers having a diameter up to about 25,000 nanometers.
2. The method of claim 1, further comprising the step of:
feeding a cleaner gas through an outer gas column, which is positioned concentrically around and apart from the annular column, where the cleaner gas exits the outer gas column at a cleaner orifice that is positioned approximate to the exit orifice, the exit of the cleaner as thereby preventing the build-up of residual amounts of fiber-forming material and/or additive at the exit orifice.
3. The method of claim 1, further comprising the step of:
feeding a shroud gas into a shroud column, which is positioned concentrically around and apart from the annular column, where the shroud gas exits the shroud orifice that surrounds the exit orifice, the exit of the shroud gas thereby controlling the cooling rate of the fiber-forming material and/or the additive being ejected from the exit orifice.

4. The method of claim 1, further comprising the step of:
directing the plurality of strands of the at least one fiber-forming material and at least one additive exiting from the exit orifice into an electric field.
5. The method of claim 1, wherein the nanofibers have a diameter in the range of above 1 nanometer to about 5,000 nanometers.
6. The method of claim 1, wherein the at least one fiber-forming material and the at least one additive are provided in combination with one another.
7. The method of claim 1, wherein the at least one fiber-forming material and the at least one additive are provided independently of one another.
8. The method of claim 1, wherein the at least one additive is selected from one or more pesticides, fungicides, anti-bacterials, fertilizers, vitamins, hormones, chemical and/or biological indicators, protein, growth factors, growth inhibitors, antioxidants, dyes, colorants, sweeteners, flavoring compounds, deodorants, or combinations of two or more thereof.
9. A method for forming a plurality of nanofibers from a single nozzle comprising the steps of:
 - (A) providing a nozzle, the nozzle comprising:
 - a center tube;
 - a first supply tube that is positioned concentrically around and apart from the center tube, wherein the center tube and the first supply tube form a first annular column, and wherein the center tube is positioned within the first supply tube so that a first gas jet space is created between a lower end of the center tube and a lower end of the supply tube;
 - a middle gas tube positioned concentrically around and apart from the first supply tube, forming a second annular column; and

a second supply tube positioned concentrically around and apart from the middle gas tube, wherein the middle gas tube and second supply tube form a third annular column, and wherein the middle gas tube is positioned within the second supply tube so that a second gas jet space is created between a lower end of the middle gas tube and a lower end of the second supply tube;

(B) feeding at least one combination of at least one fiber-forming material and at least one additive into the first and second supply tubes;

(C) directing the at least one combination of at least one fiber-forming material and at least one additive into the first and second gas jet spaces, thereby forming an annular film of the at least one fiber-forming material and the at least one additive in the first and second gas jet spaces, each annular film having an inner circumference; and

(D) simultaneously forcing gas through the center tube and the middle gas tube, and into the first and second gas jet spaces, thereby causing the gas to contact the inner circumference of the annular films in the first and second gas jet spaces, and ejecting the at least one fiber-forming material and the at least one additive from the exit orifices of the first and third annular columns in the form of a plurality of strands of fiber-forming material and additive that solidify and form nanofibers having a diameter up to about 25,000 nanometers.

10. The method of claim 9, wherein the at least one additive is selected from one or more pesticides, fungicides, anti-bacterials, fertilizers, vitamins, hormones, chemical and/or biological indicators, protein, growth factors, growth inhibitors, antioxidants, dyes, colorants, sweeteners, flavoring compounds, deodorants, or combinations of two or more thereof.

11. The method of claim 9, wherein the at least one additive is selected from one or more nitric oxide-releasing compounds.

12. The process of claim 9, wherein the nanofibers have a diameter in the range of above 1 nanometer to about 5,000 nanometers.

13. The method of claim 9, wherein the nozzle additionally contains an outer gas tube having an inlet orifice and outlet orifice, the outer gas tube being positioned concentrically around and apart from an outermost supply tube, and wherein the method further comprises the step of feeding a cleaner gas through the outer gas column, where the cleaner gas exits the outer gas column at a cleaner orifice that is positioned proximate to an exit orifice of the outermost supply tube, wherein the exit of the cleaner gas thereby prevents the build-up of residual amounts of fiber-forming material at the exit orifice of the outermost supply tube.

14. The method of claim 13, wherein the nozzle additionally contains a shroud gas tube positioned concentrically around and apart from the outer gas tube, the shroud gas tube having an inlet orifice and an outlet orifice, and wherein the method further comprises the step of feeding a shroud gas into the shroud gas tube, such that shroud gas exits the shroud gas tube from the shroud gas tube exit orifice, the exit of the shroud gas thereby influencing the solidification rate of the fiber-forming material being ejected from the exit orifices of the supply tubes.

15. The method of claim 13, further comprising the step of supplying at least one electric charge to at least one of the nozzle, the at least one fiber-forming material, the at least one additive, or a portion of the nozzle, wherein the at least one electrical charge creates an electric field in or around the nanofibers.

16. The method of claim 15, further comprising one or more external electric fields for use in controlling the nanofibers.

17. A method for forming a plurality of nanofibers from a single nozzle comprising the steps of:

(A) providing a nozzle, the nozzle comprising:

a center tube;

a first supply tube that is positioned concentrically around and apart from the center tube, wherein the center tube and the first supply tube form a first annular column, and wherein the center tube is positioned within the first supply tube

so that a first gas jet space is created between a lower end of the center tube and a lower end of the supply tube;

a middle gas tube positioned concentrically around and apart from the first supply tube, forming a second annular column; and

a second supply tube positioned concentrically around and apart from the middle gas tube, wherein the middle gas tube and second supply tube form a third annular column, and wherein the middle gas tube is positioned within the second supply tube so that a second gas jet space is created between a lower end of the middle gas tube and a lower end of the second supply tube;

(B) feeding at least one fiber-forming material and at least one additive into the first and second supply tubes;

(C) directing the at least one fiber-forming material and at least one additive into the first and second gas jet spaces, thereby forming an annular film of the at least one fiber-forming material and the at least one additive in the first and second gas jet spaces, each annular film having an inner circumference; and

(D) simultaneously forcing gas through the center tube and the middle gas tube, and into the first and second gas jet spaces, thereby causing the gas to contact the inner circumference of the annular films in the first and second gas jet spaces, and ejecting the at least one fiber-forming material and the at least one additive from the exit orifices of the first and third annular columns in the form of a plurality of strands of fiber-forming material and additive that solidify and form nanofibers having a diameter up to about 25,000 nanometers.

18. The method of claim 17, wherein the at least one additive is selected from one or more pesticides, fungicides, anti-bacterials, fertilizers, vitamins, hormones, chemical and/or biological indicators, protein, growth factors, growth inhibitors, antioxidants, dyes, colorants, sweeteners, flavoring compounds, deodorants, or combinations of two or more thereof.

19. The method of claim 17, wherein the at least one additive is selected from one or more nitric oxide-releasing compounds.

20. The method of claim 17, wherein the at least one additive is in the form of molecules, particles, a coating, a separated phase, gel particles, small gas bubbles, and/or liquid droplets that are sequestered on, in or about the nanofibers.

21. The process of claim 17, wherein the nanofibers have a diameter in the range of above 1 nanometer to about 5,000 nanometers.

22. The method of claim 17, wherein the nozzle additionally contains an outer gas tube having an inlet orifice and outlet orifice, the outer gas tube being positioned concentrically around and apart from an outermost supply tube, and wherein the method further comprises the step of feeding a cleaner gas through the outer gas column, where the cleaner gas exits the outer gas column at a cleaner orifice that is positioned proximate to an exit orifice of the outermost supply tube, wherein the exit of the cleaner gas thereby prevents the build-up of residual amounts of fiber-forming material at the exit orifice of the outermost supply tube.

23. The method of claim 22, wherein the nozzle additionally contains a shroud gas tube positioned concentrically around and apart from the outer gas tube, the shroud gas tube having an inlet orifice and an outlet orifice, and wherein the method further comprises the step of feeding a shroud gas into the shroud gas tube, such that shroud gas exits the shroud gas tube from the shroud gas tube exit orifice, the exit of the shroud gas thereby influencing the solidification rate of the fiber-forming material being ejected from the exit orifices of the supply tubes.

24. The method of claim 22, further comprising the step of supplying at least one electric charge to at least one of the nozzle, the at least one fiber-forming material, the at least one additive, or a portion of the nozzle, wherein the at least one electrical charge creates an electric field in or around the nanofibers.

25. The method of claim 24, further comprising one or more external electric fields for use in controlling the nanofibers.

1/5

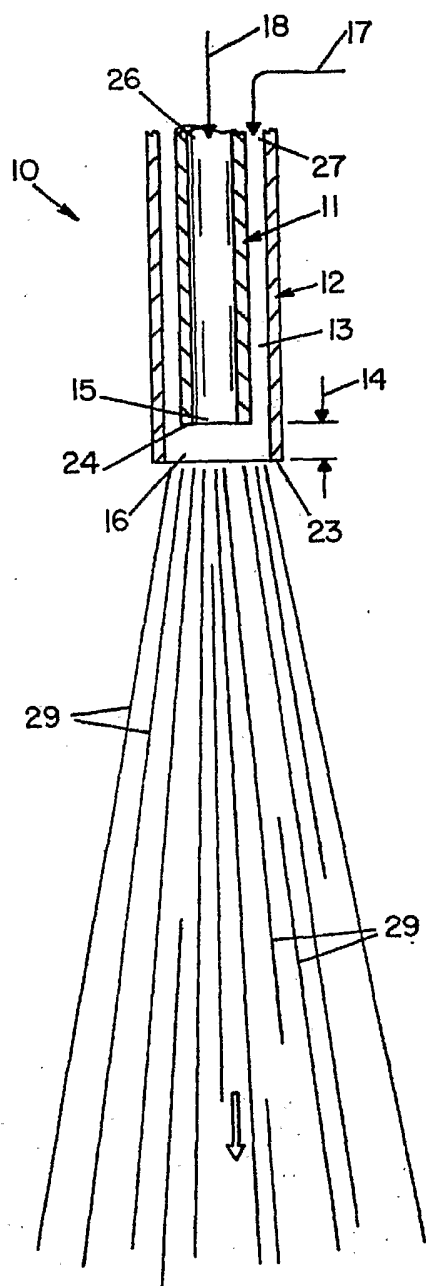


FIG. 1

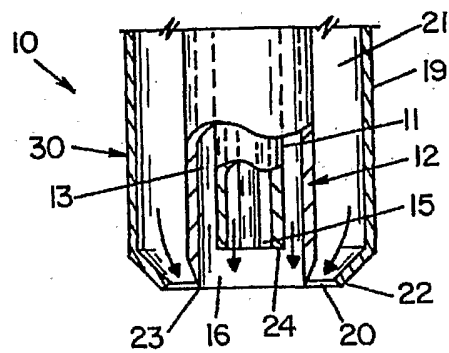


FIG. 2

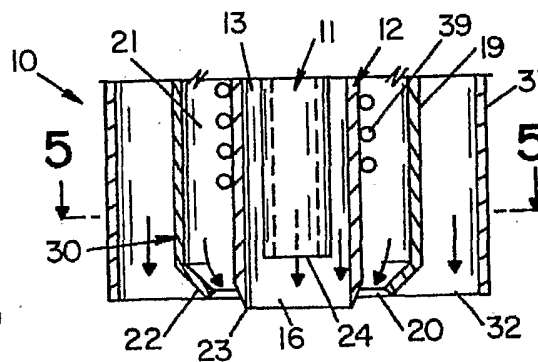


FIG. 3

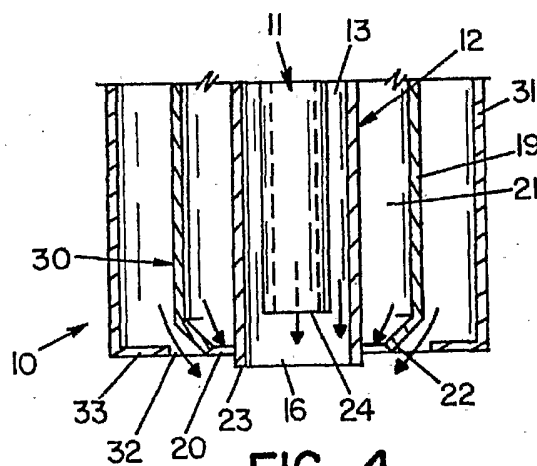


FIG. 4

2/5

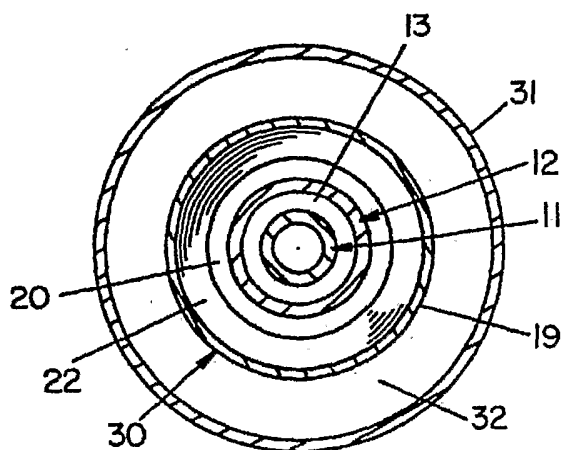


FIG. 5

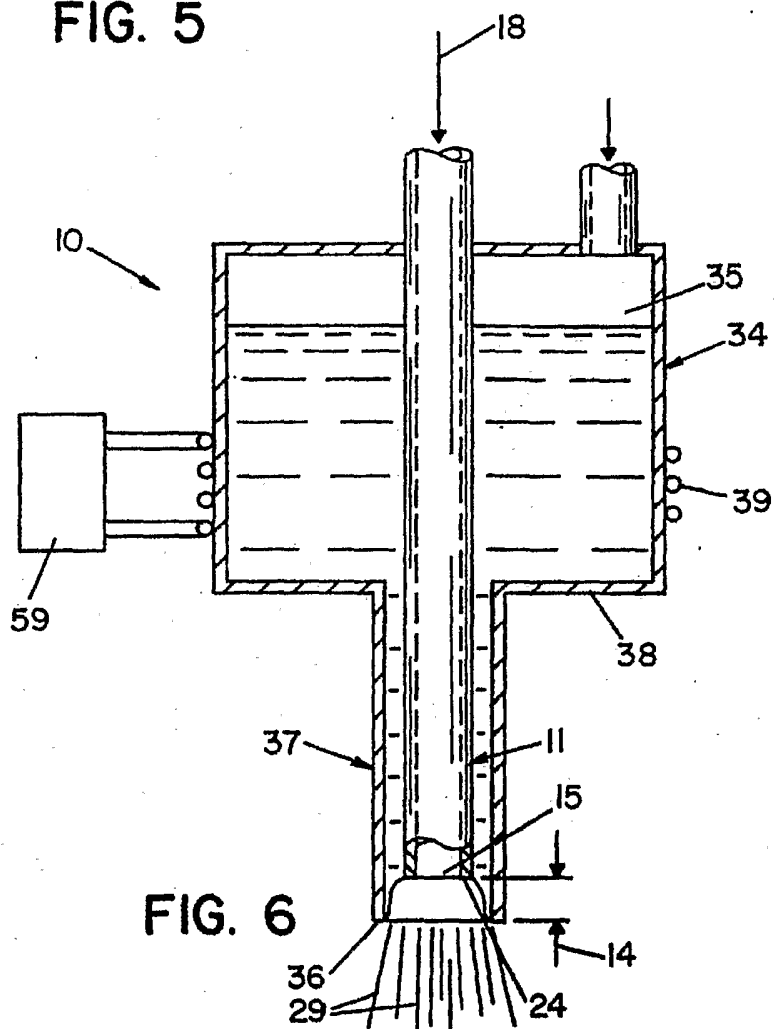


FIG. 6

3/5

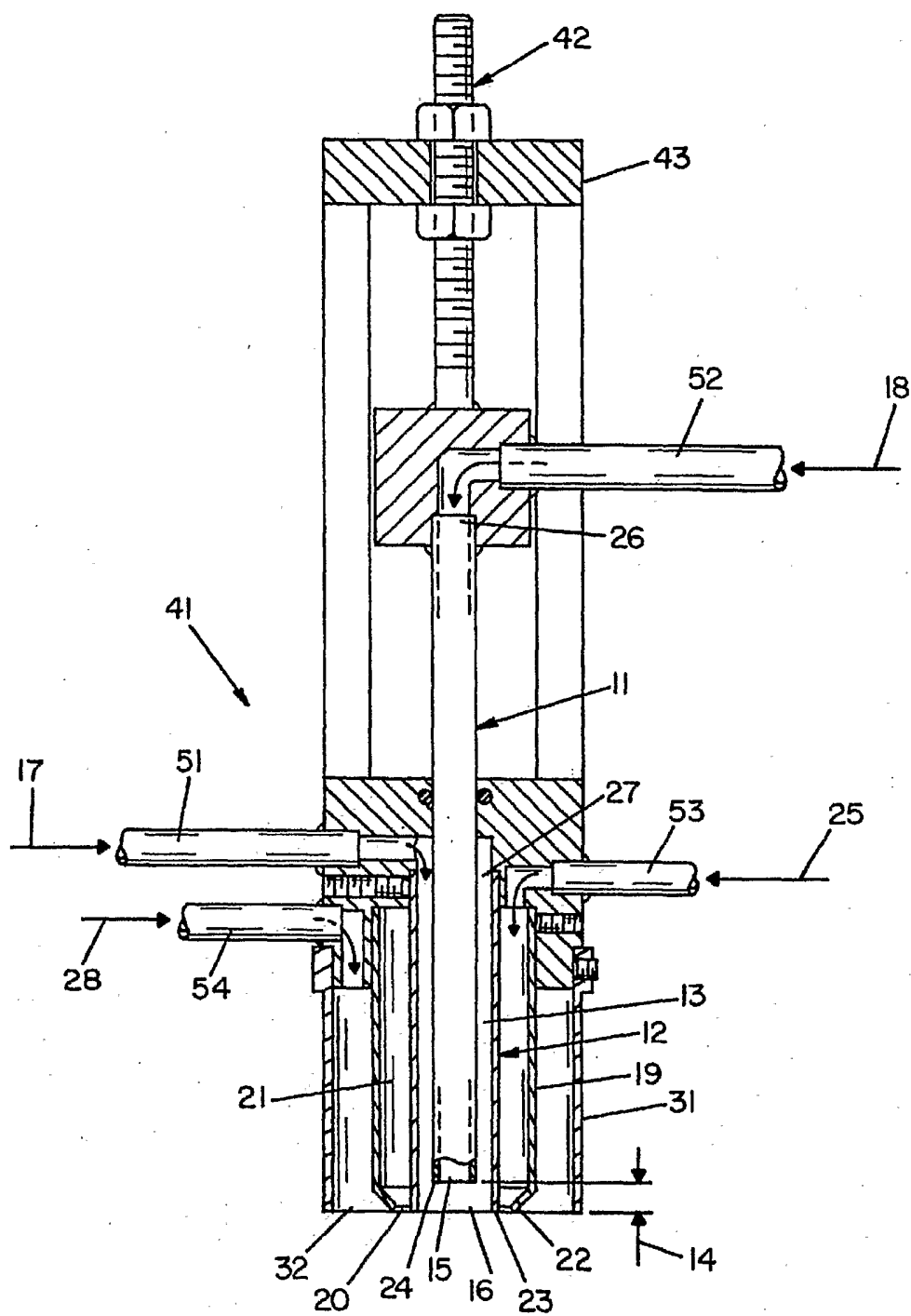


FIG. 7

4/5

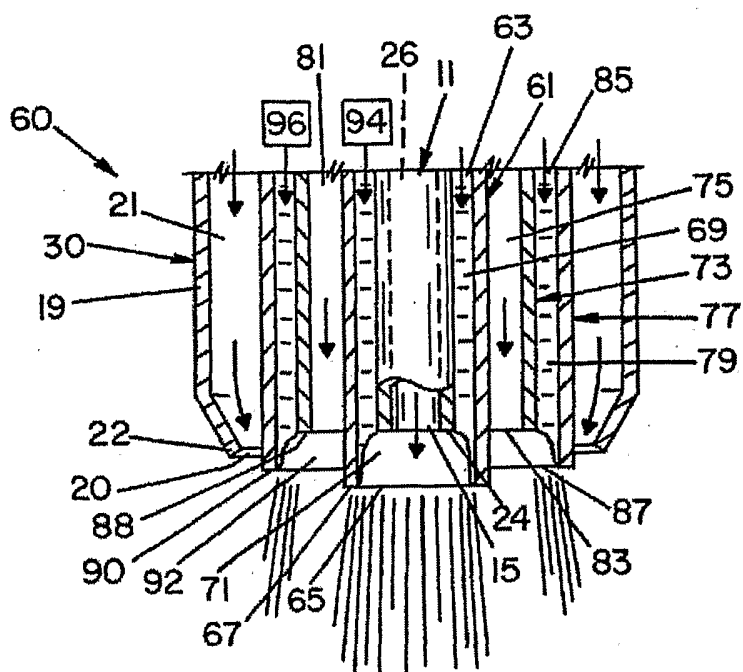


FIG. 8

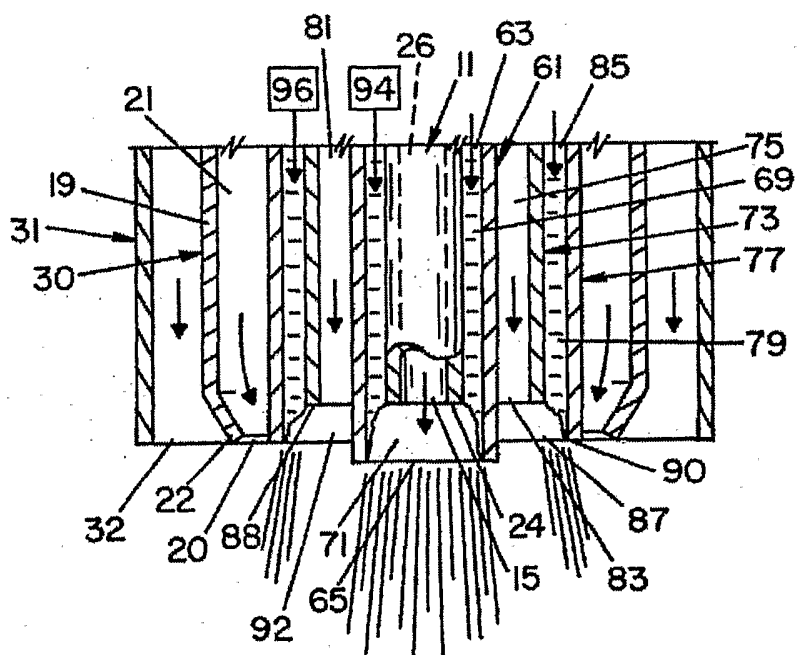


FIG. 9

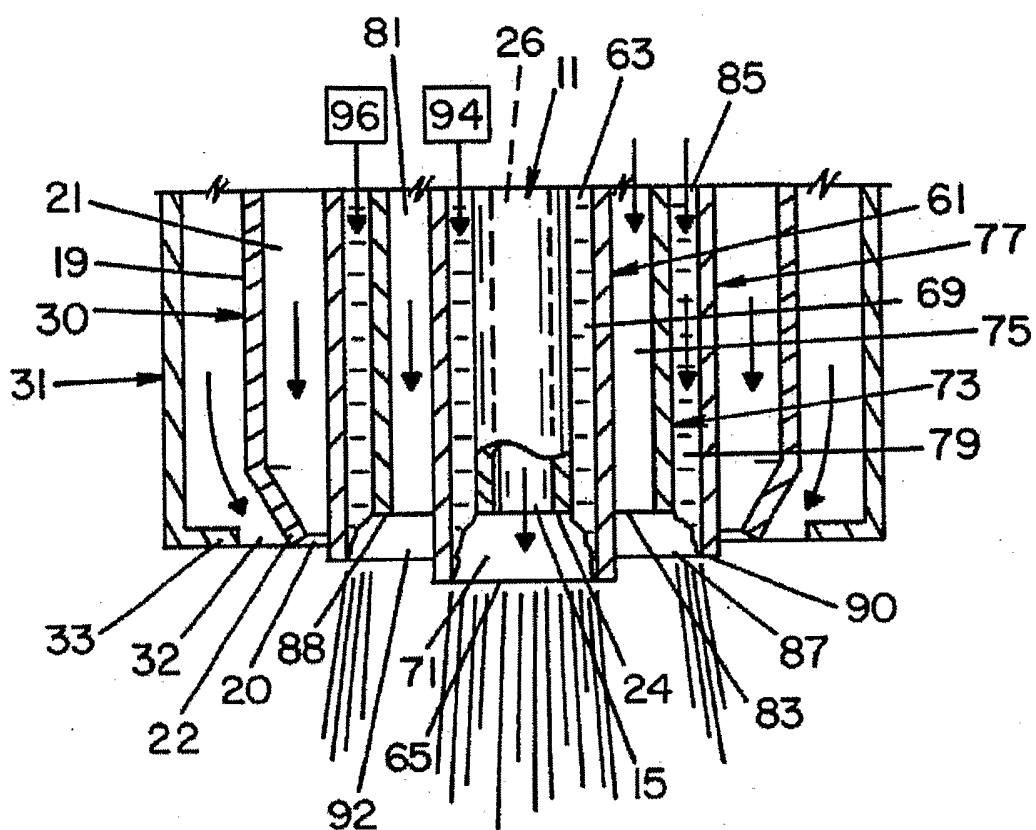


FIG. 10