US 20020084290A1

(19) **United States**
(12) **Patent Application Publication** (10) **Pub. No.: US 2002/0084290 A1**
Materna (43) **Pub. Date: Jul. 4, 2002**

(54) METHOD AND APPARATUS FOR DISPENSING SMALL VOLUME OF LIQUID, SUCH AS WITH A WETING-RESISTANT NOZZLE

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(21) Appl. No.: **10/012,102**

(22) Filed: **Nov. 13, 2001**

Related U.S. Application Data

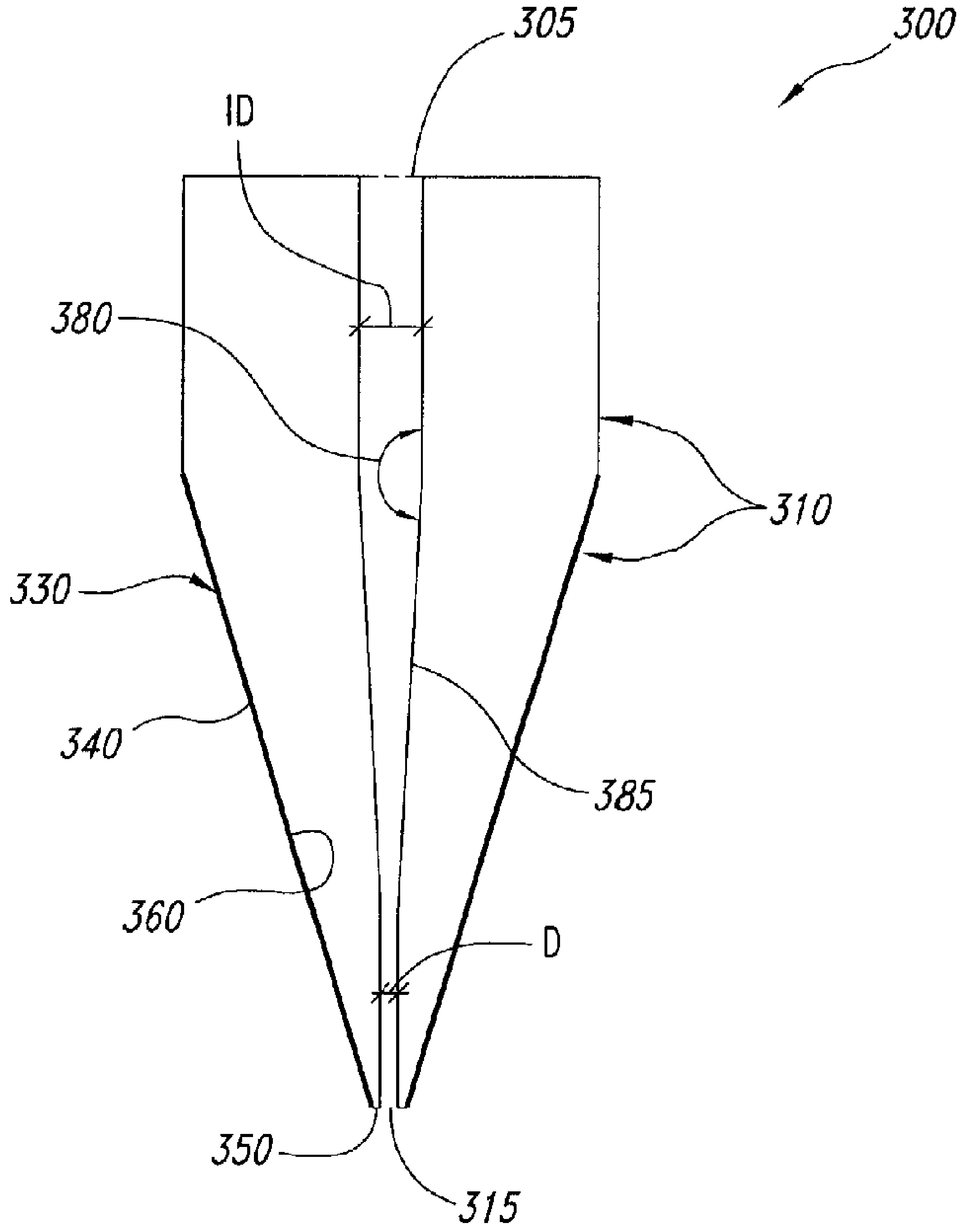
(63) Non-provisional of provisional application No. 60/247,176, filed on Nov. 10, 2000. Non-provisional of provisional application No. 60/284,783, filed on Apr. 18, 2001. Non-provisional of provisional application No. 60/288,025, filed on May 1, 2001.

Publication Classification

(51) **Int. Cl.**^{7} **B65D 47/18**
(52) **U.S. Cl.** **222/420**

(57) ABSTRACT

A wetting-resistant nozzle for accurately and precisely dispensing small volumes of liquids. The nozzle comprises an internal flowpath, and an external surface that recedes from the discharge point at an angle greater than 90 degrees, and an exceptionally low surface energy for the external surface. The low surface energy material may exist as a coating on top of a shaped substrate. A flat land region may be included and may have sharp edges, one of which may define the boundary of the low surface energy region. Another embodiment includes the low surface energy material as a bulk material through which a hole is drilled. The internal flowpath inside the nozzle may be smoothly tapered. Liquid being dispensed tends not to advance past the edge of the low surface energy region, which may coincide with a geometrically sharp edge. Such nozzles provide improved dispensing of liquids that have both low surface tension and low viscosity, such as organic solvents.



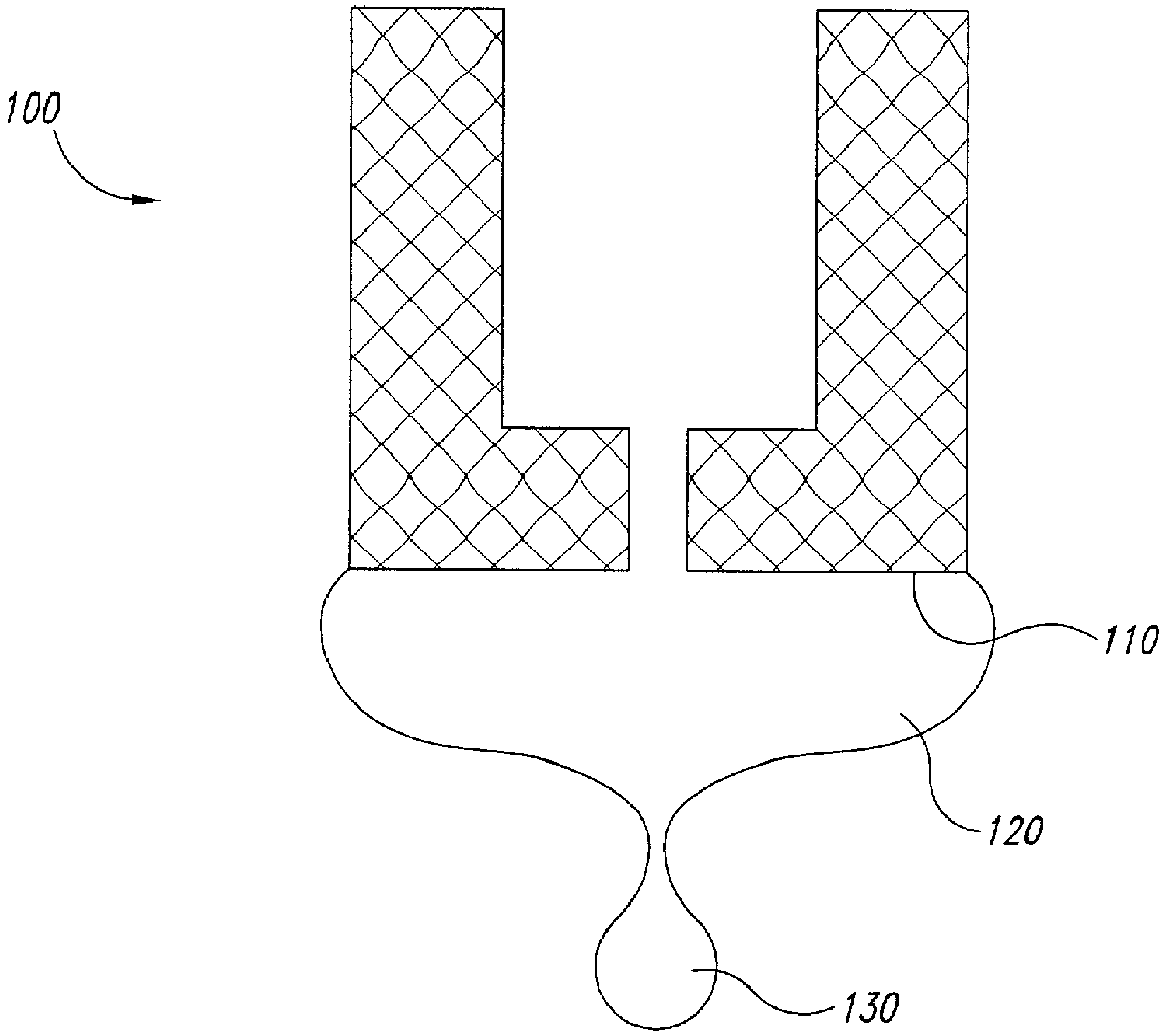


Fig. 1
(Prior Art)

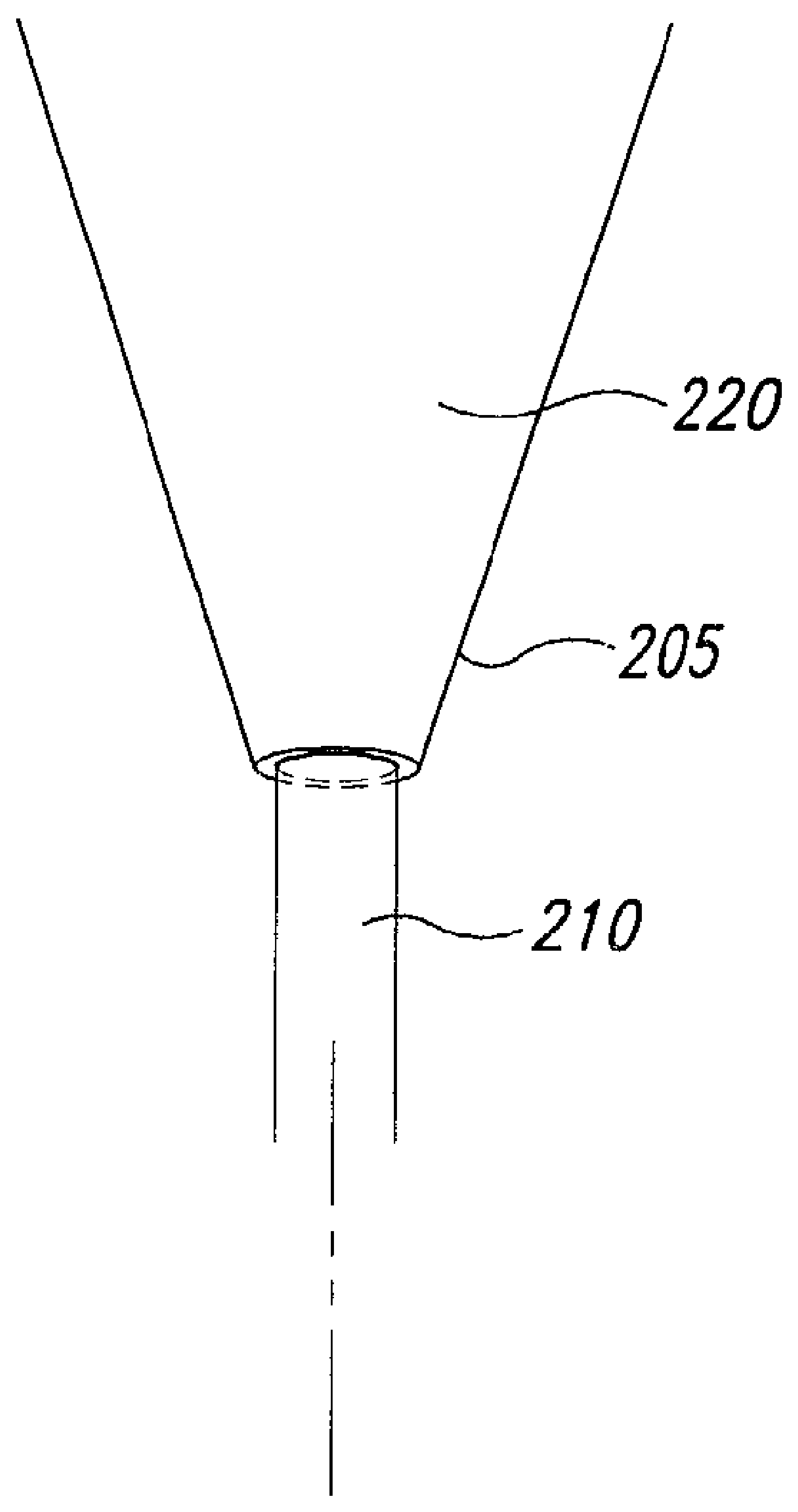


Fig. 2A
(Prior Art)

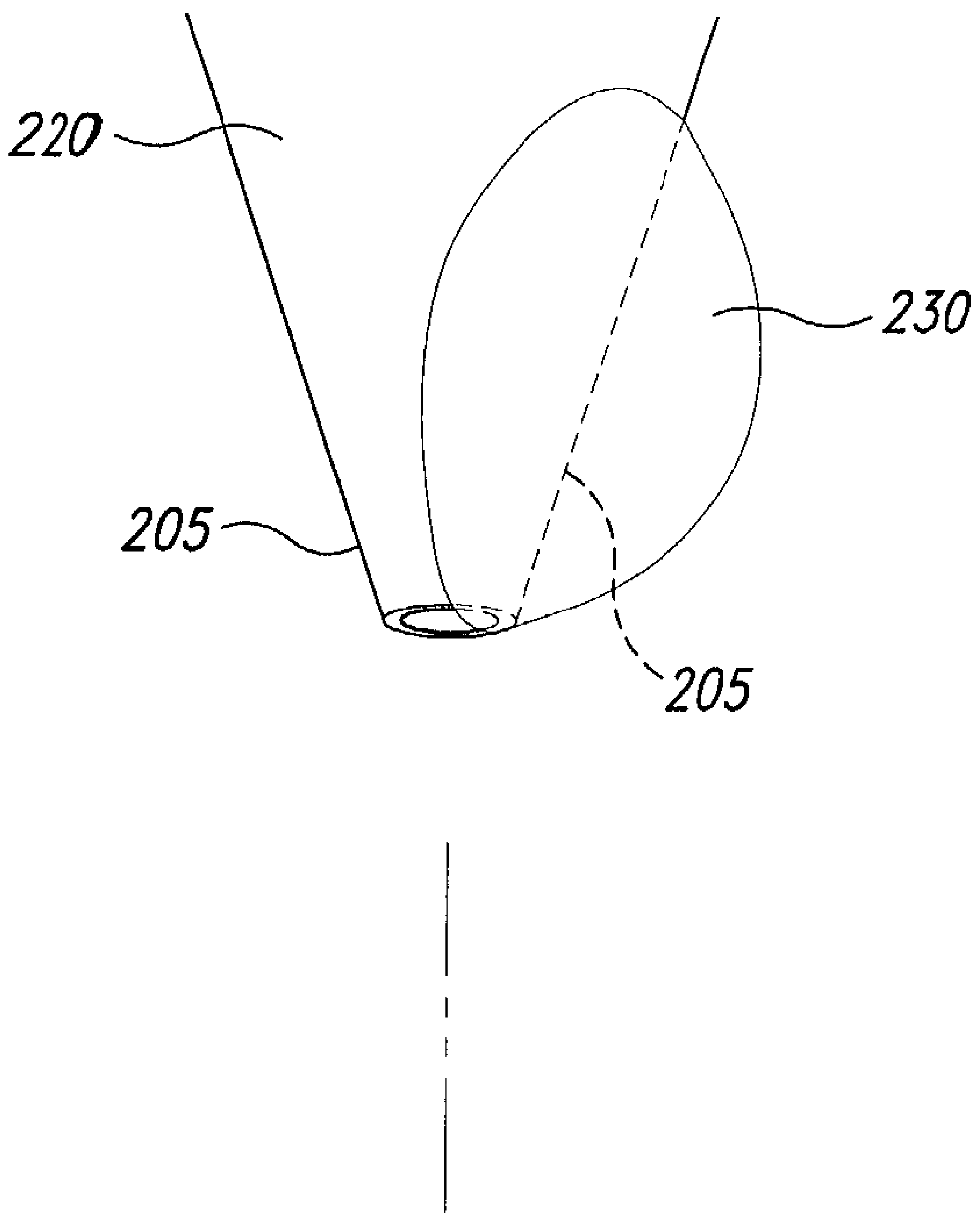


Fig. 2B
(Prior Art)

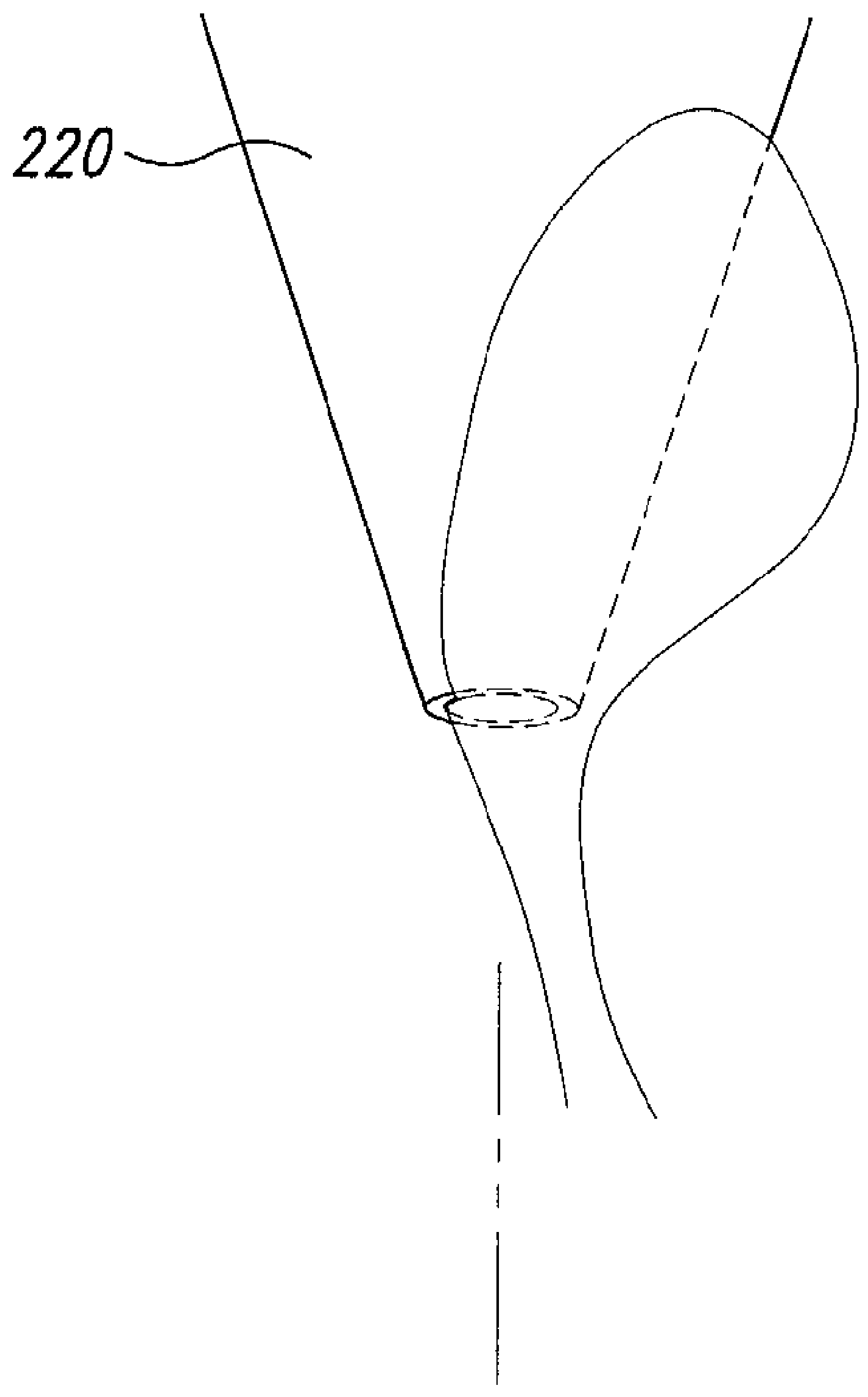


Fig. 2C
(Prior Art)

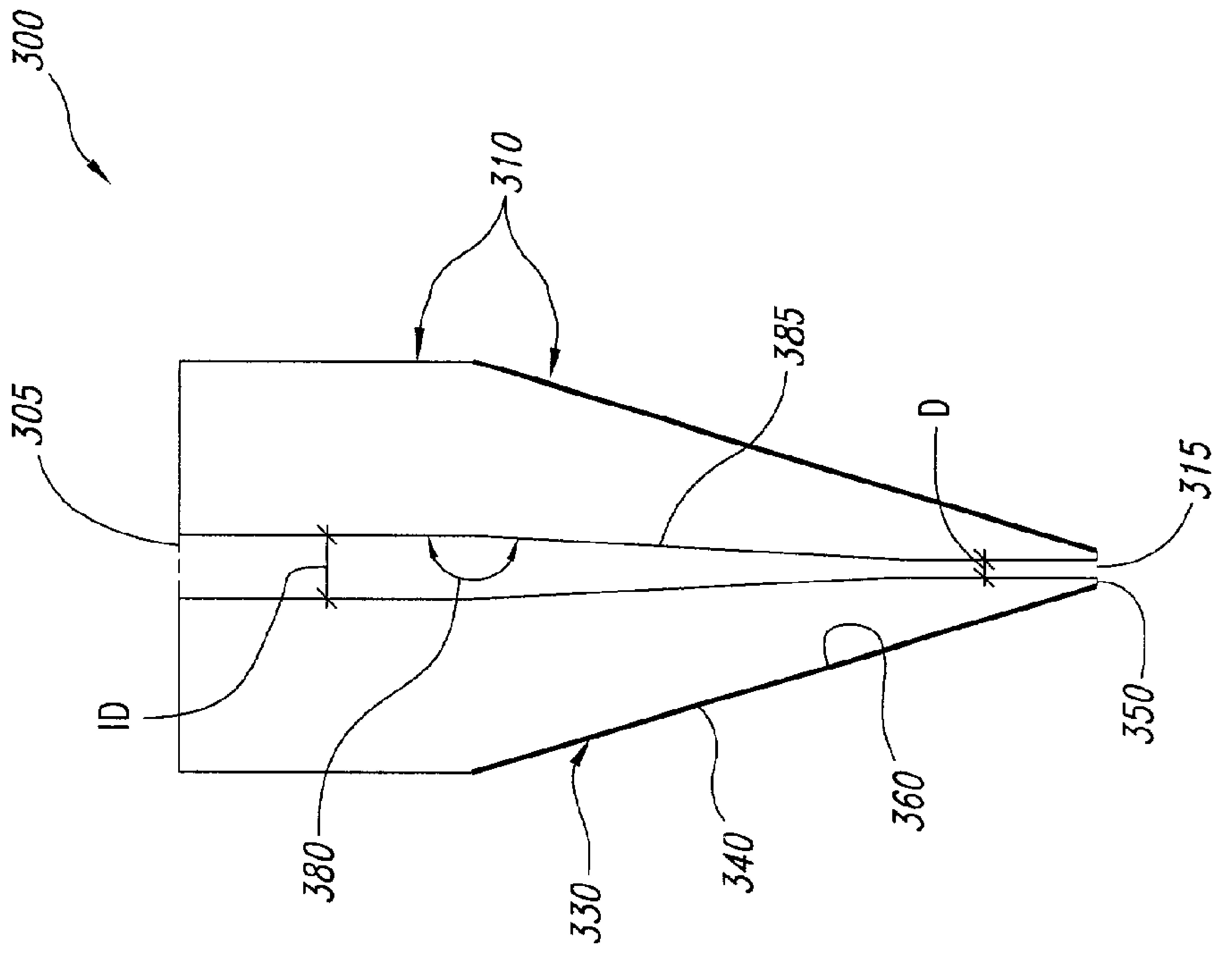

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Fig. 3

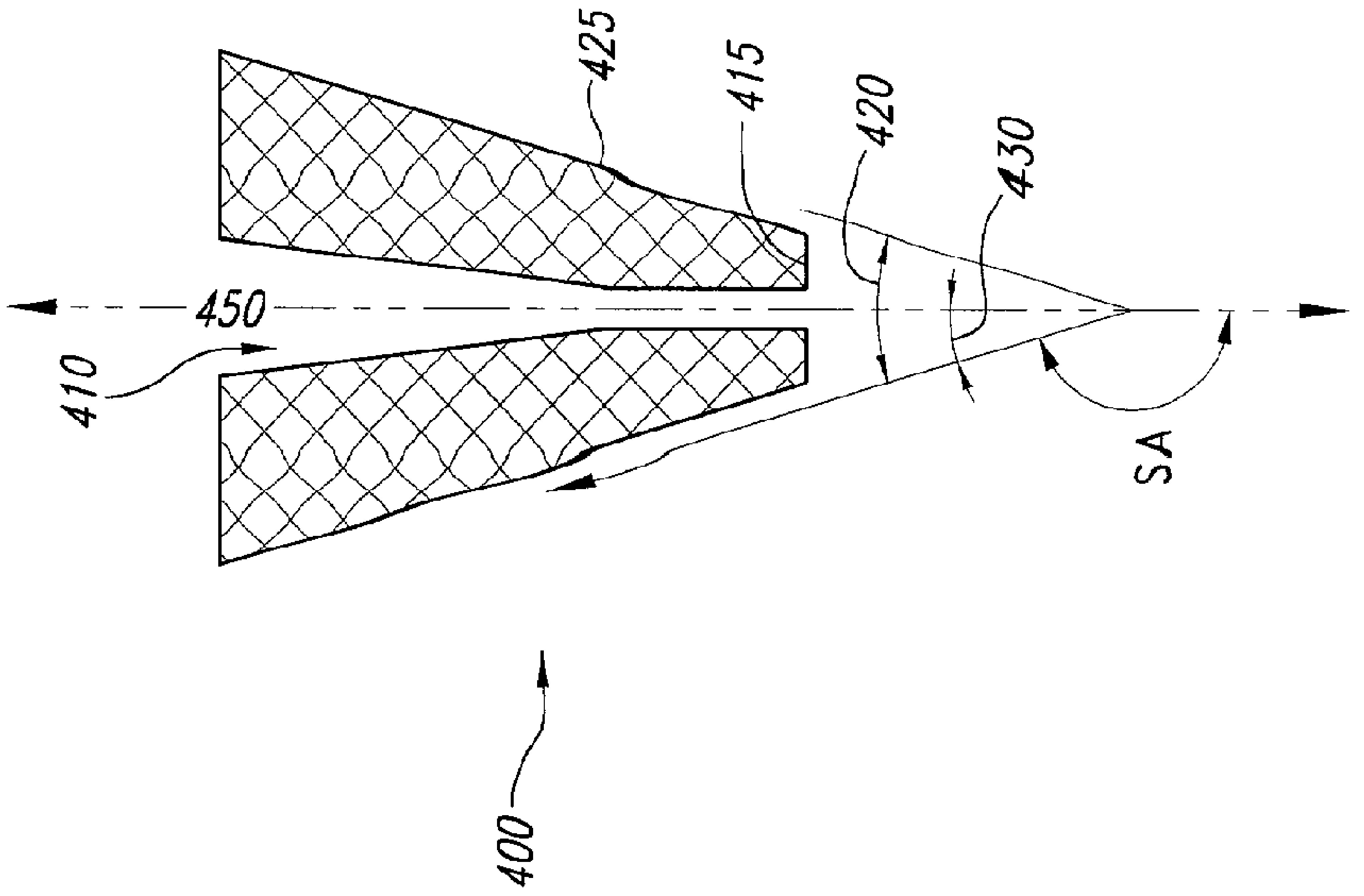
425
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Fig. 4

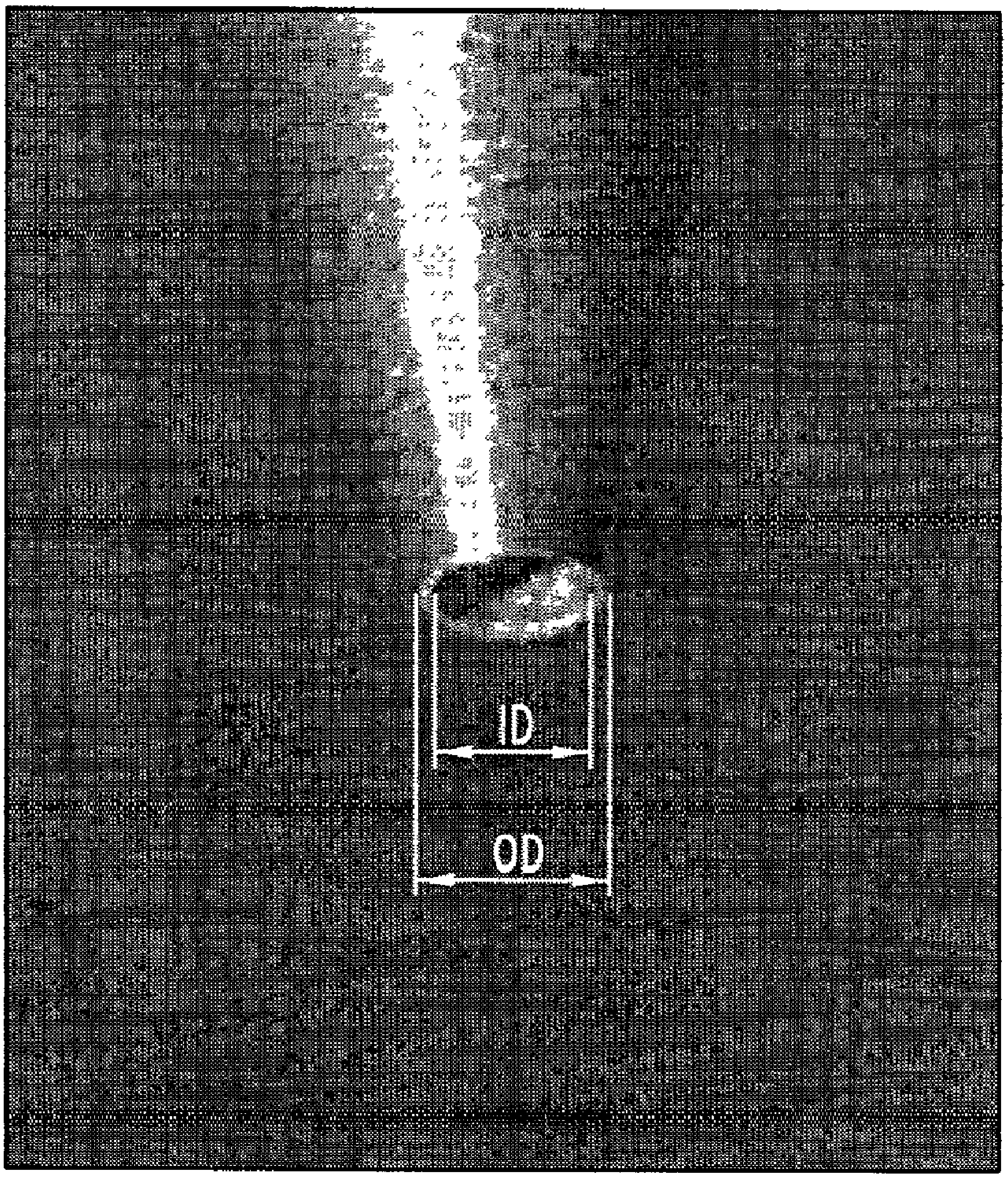

Fig. 5

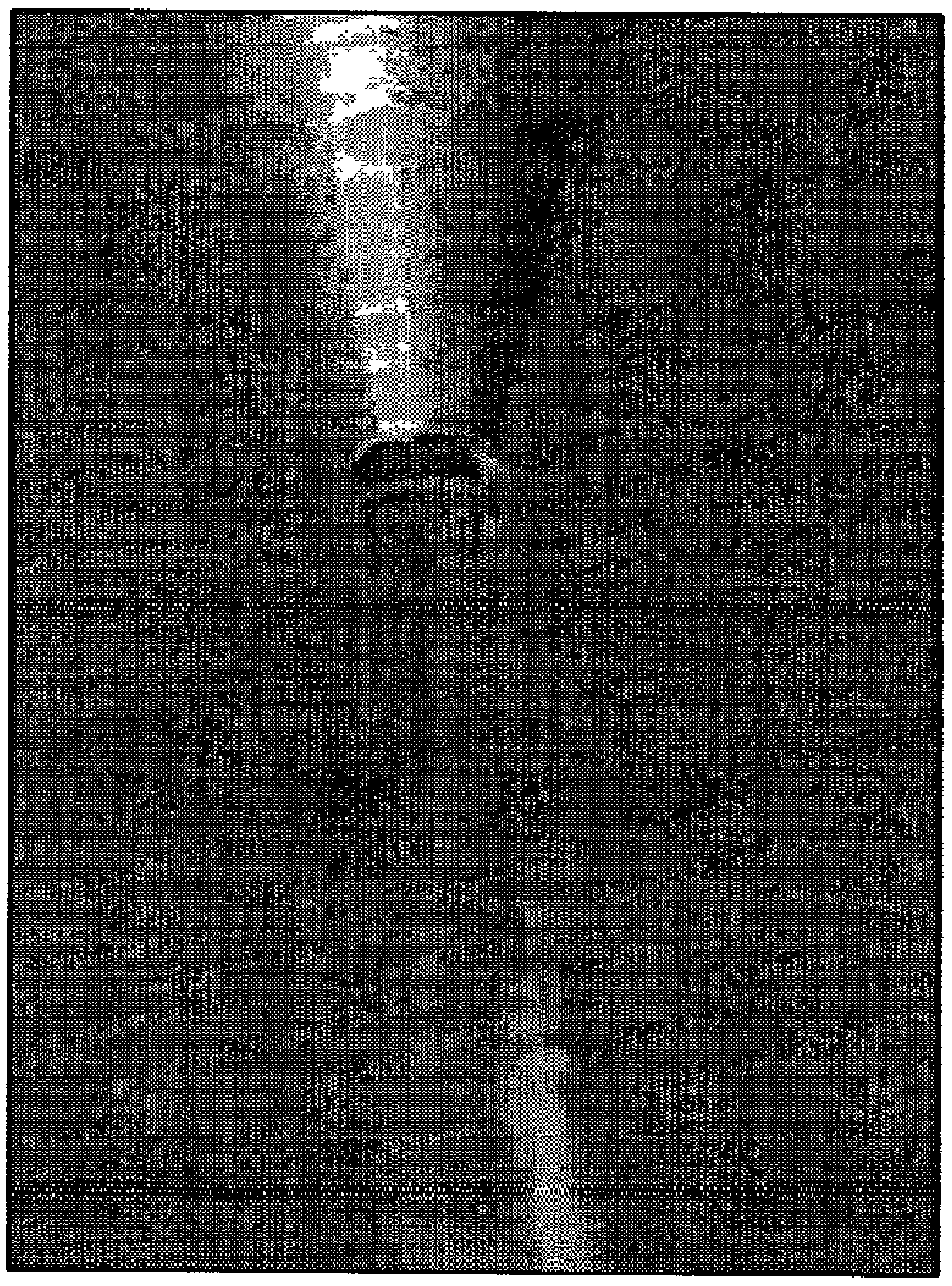

Fig. 6A

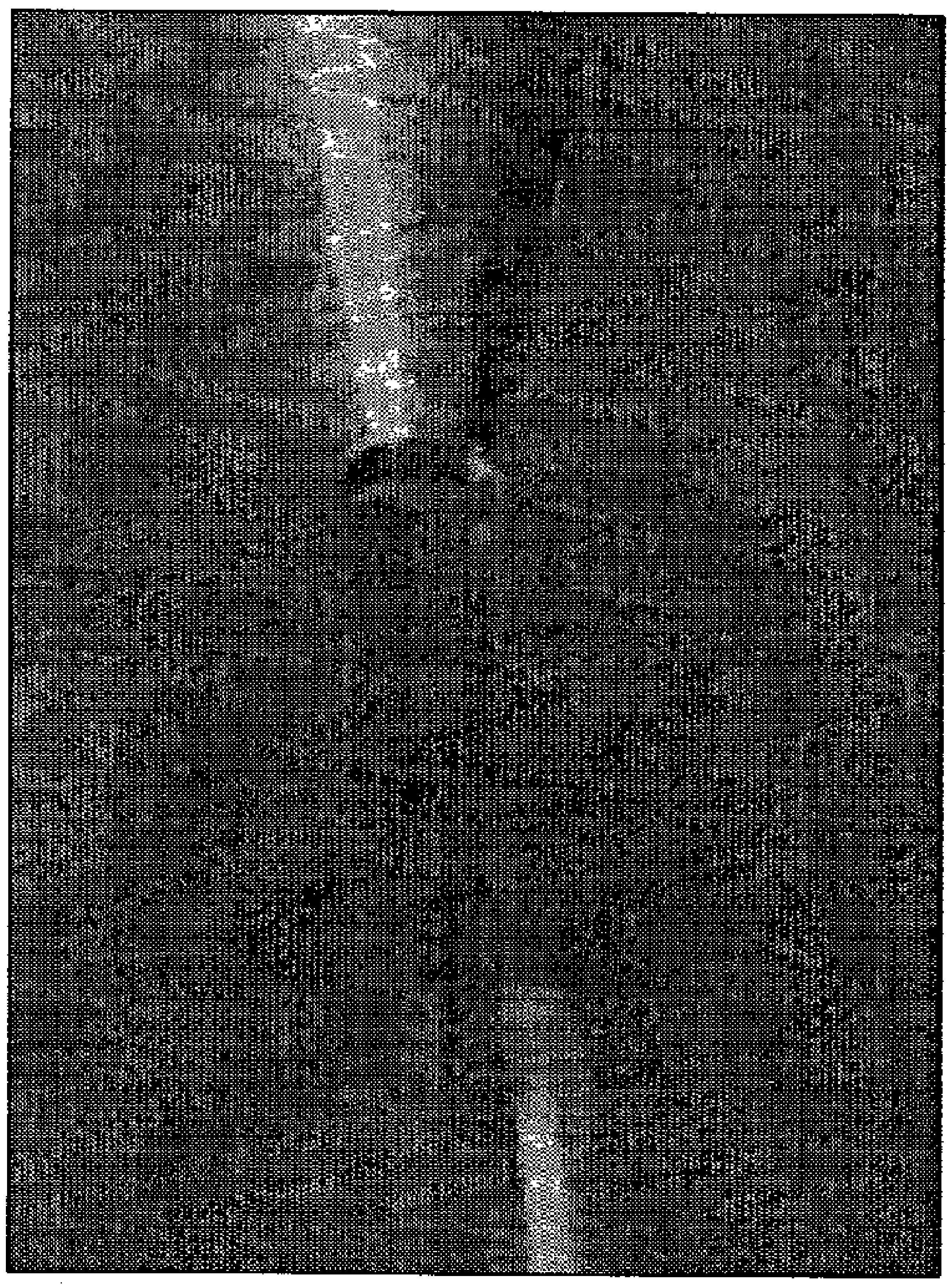

Fig. 6B

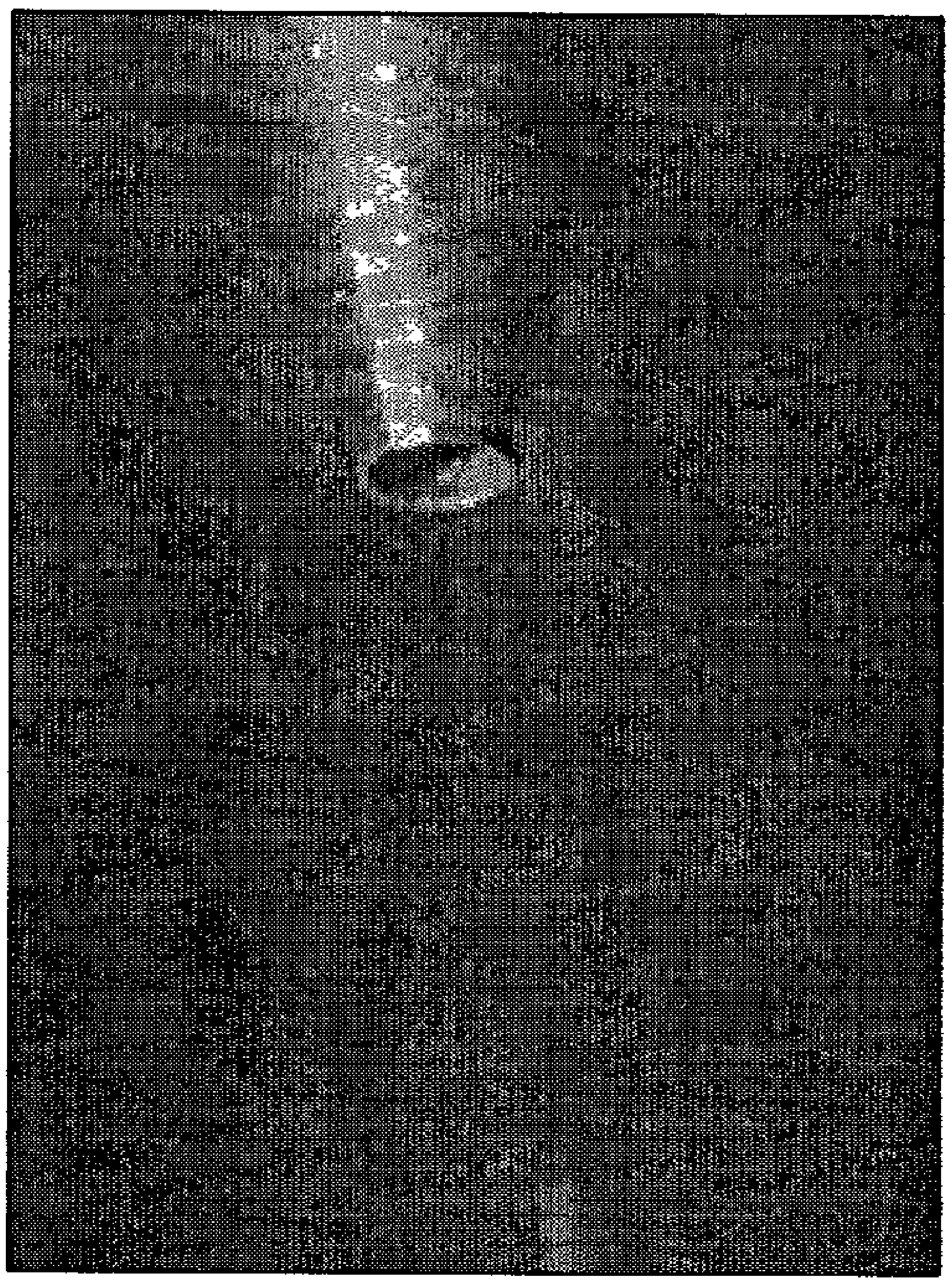

Fig. 6C

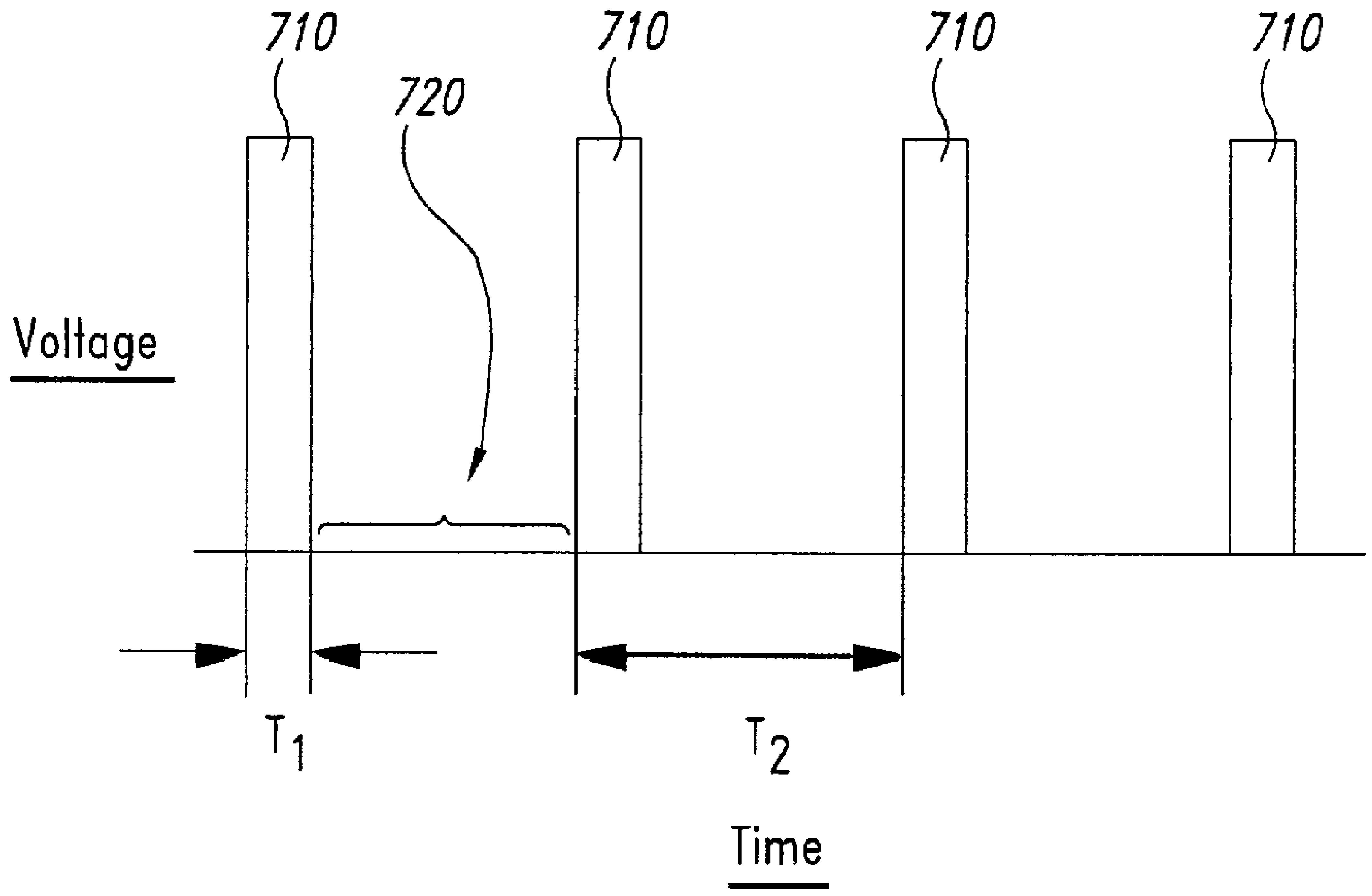

Fig. 7

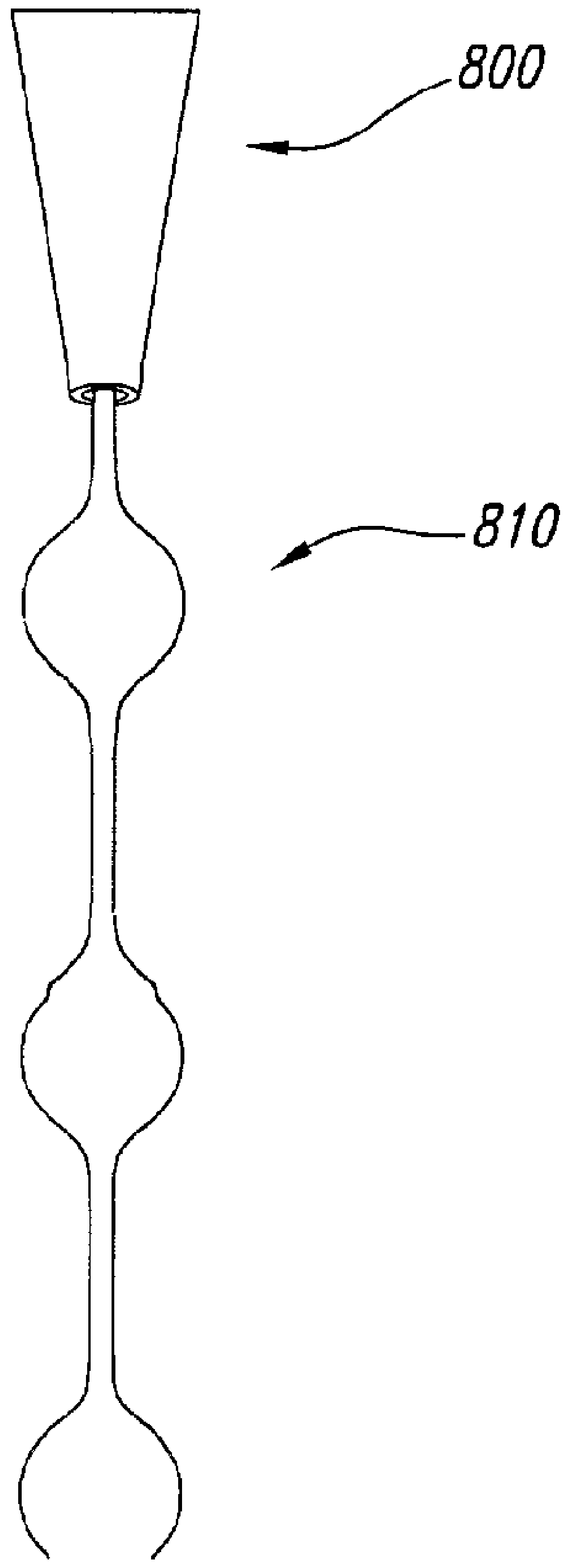

Fig. 8

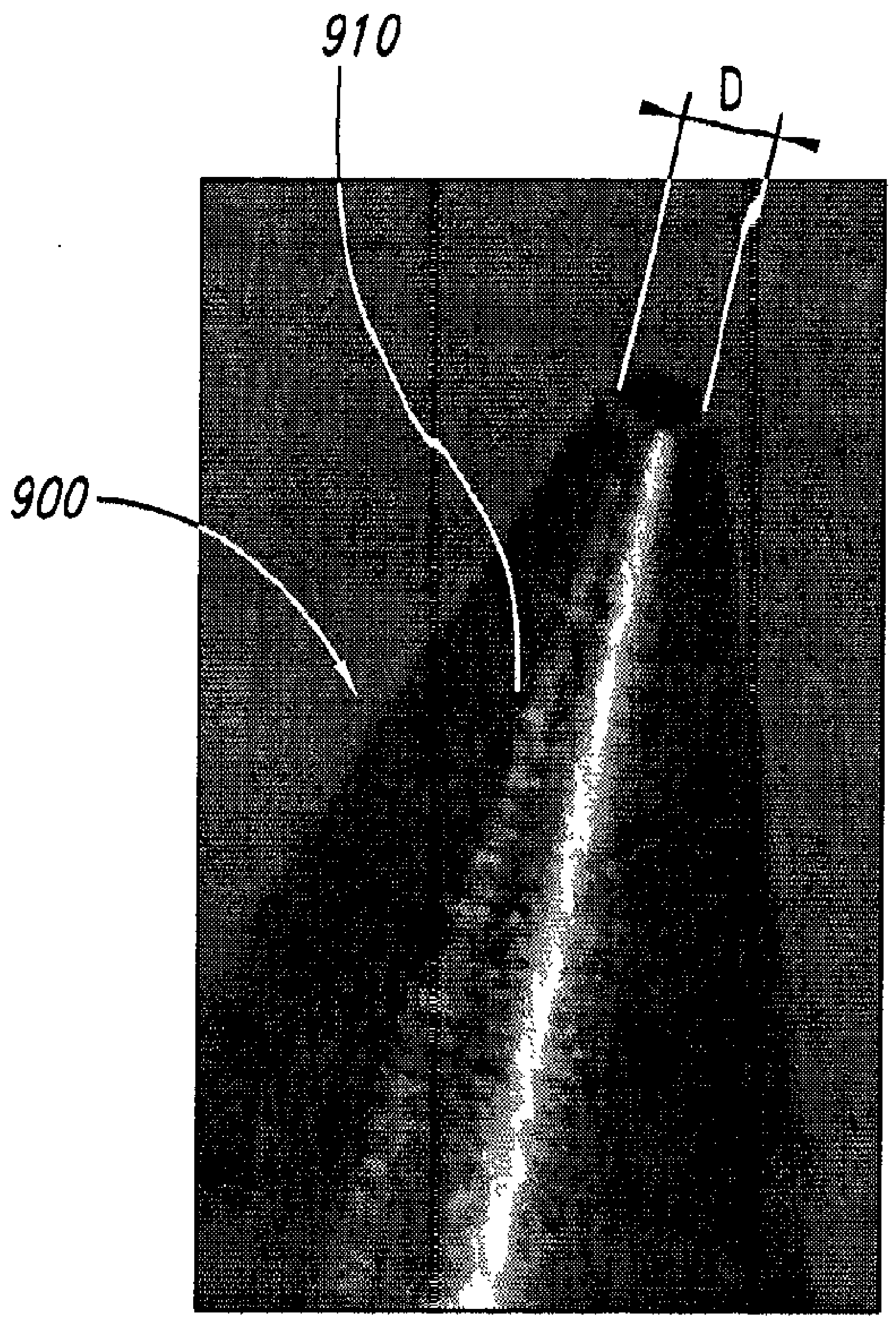

Fig. 9A

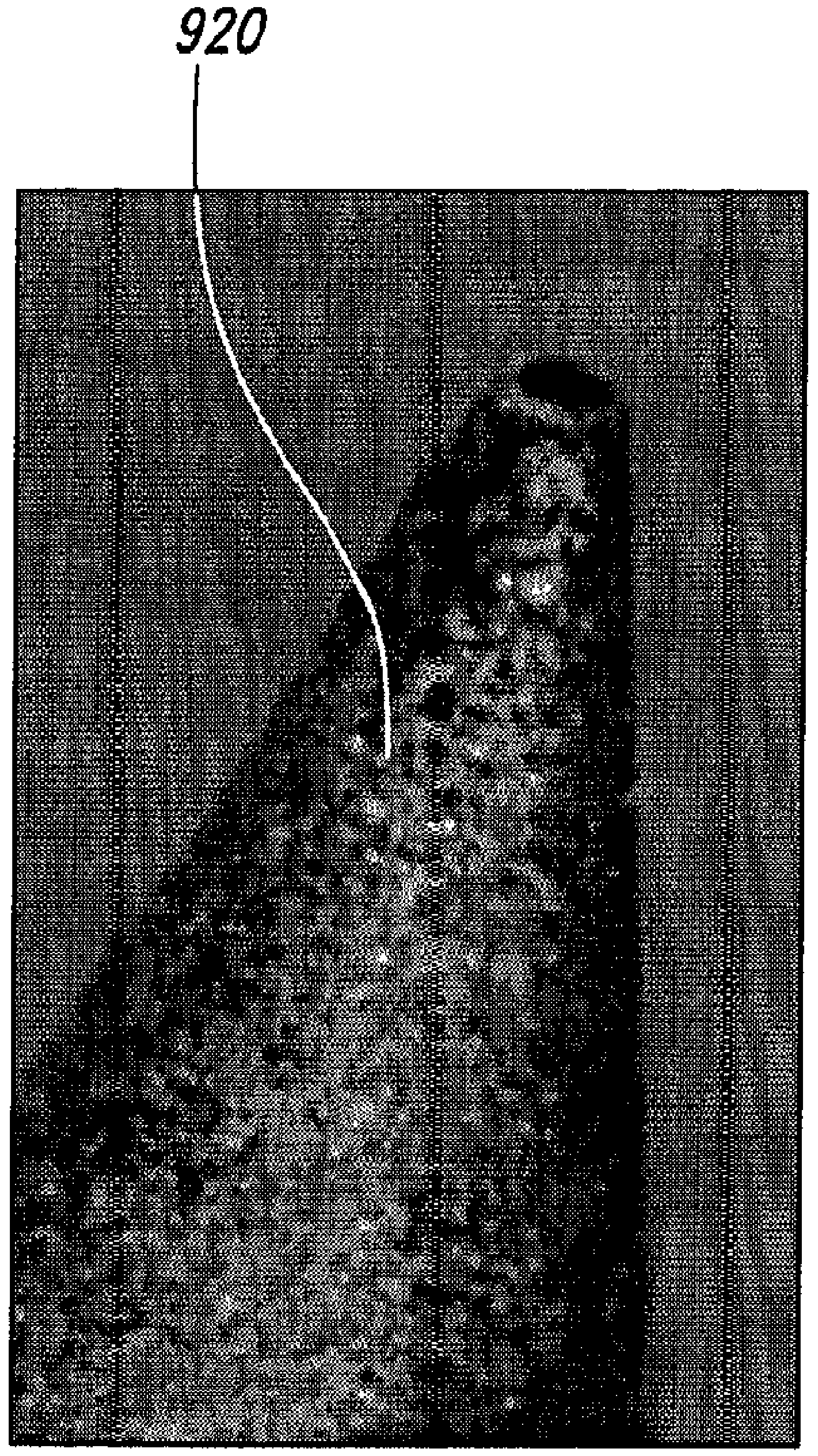

Fig. 9B

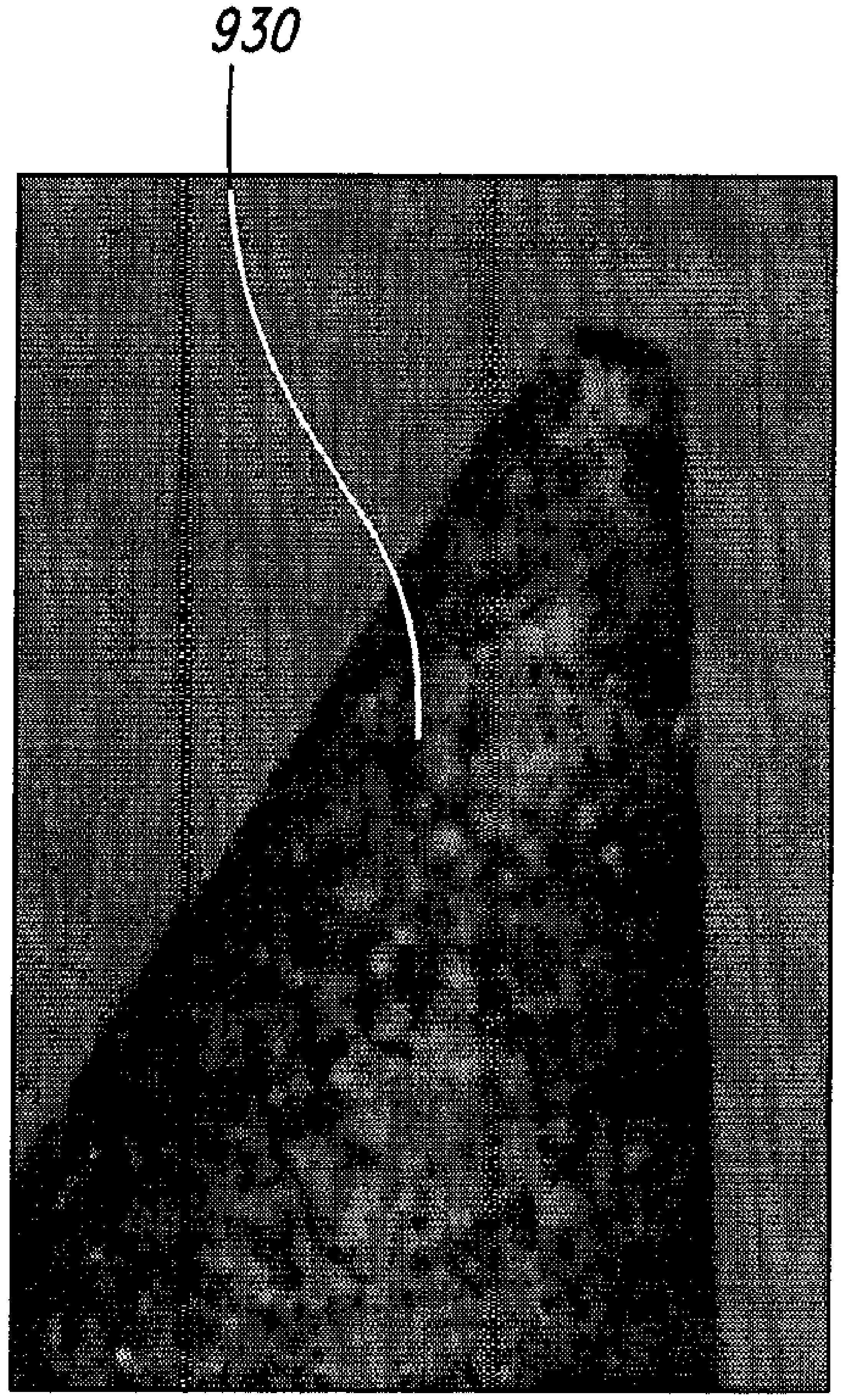

Fig. 9C

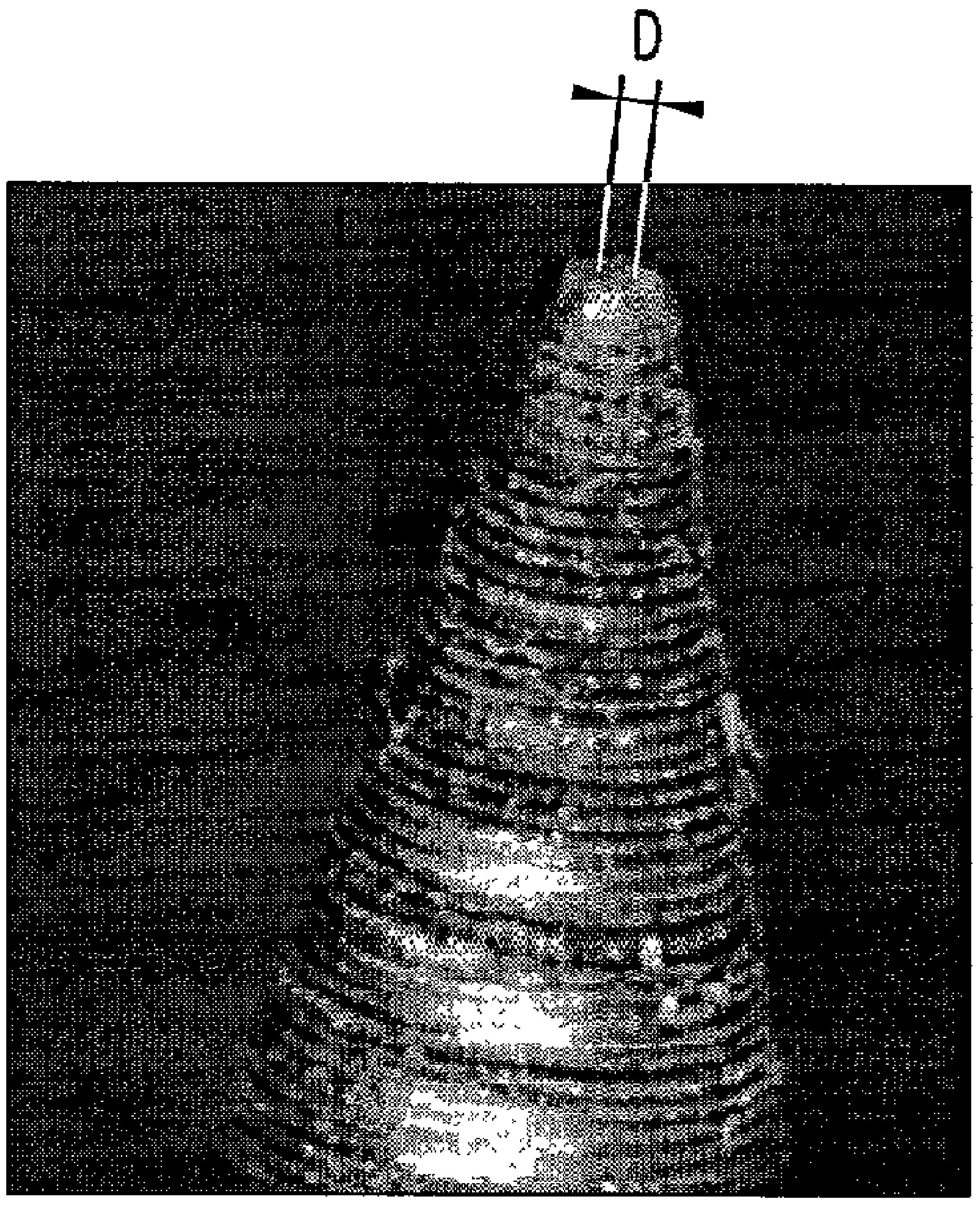

Fig. 10A

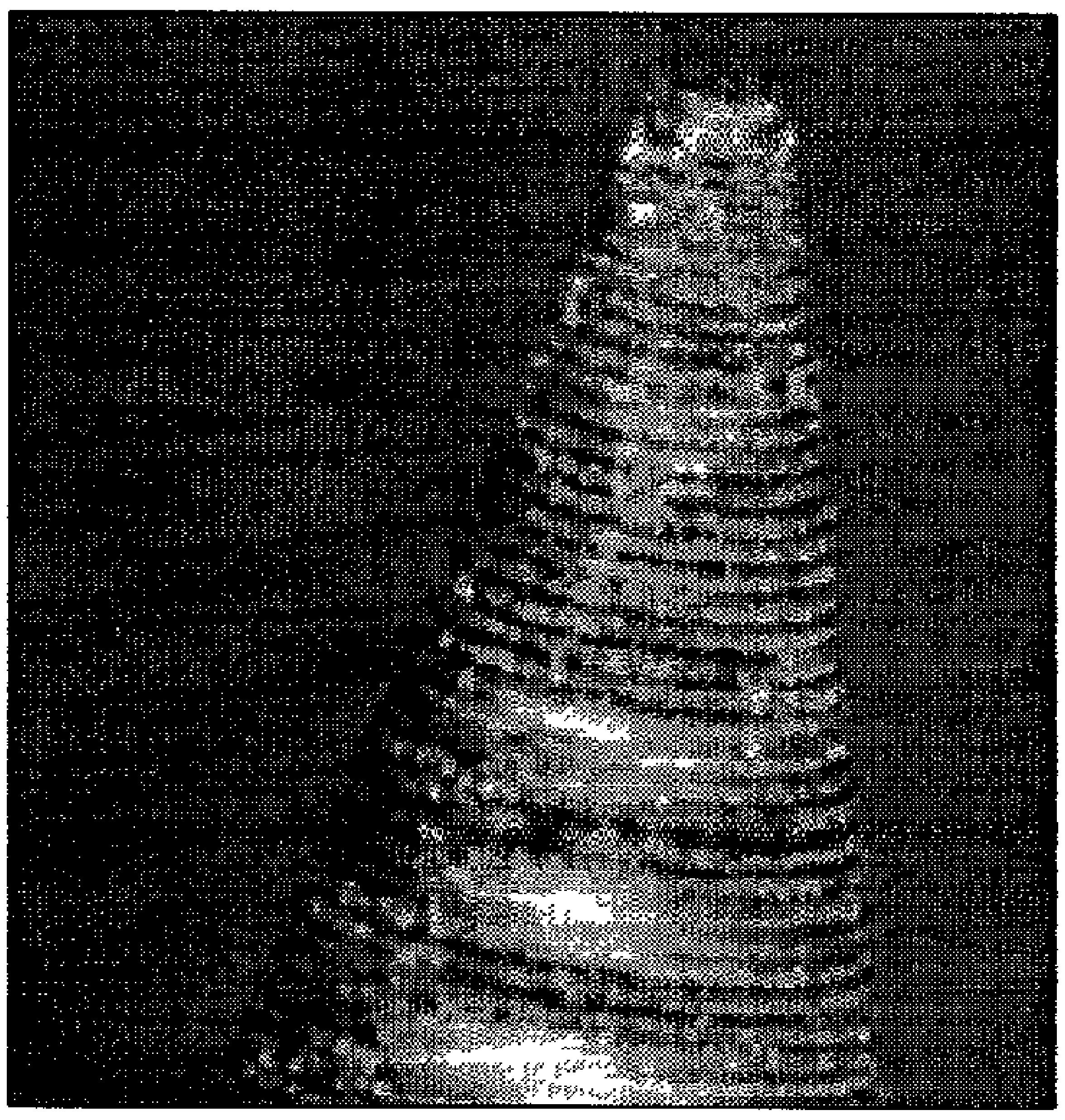

Fig. 10B

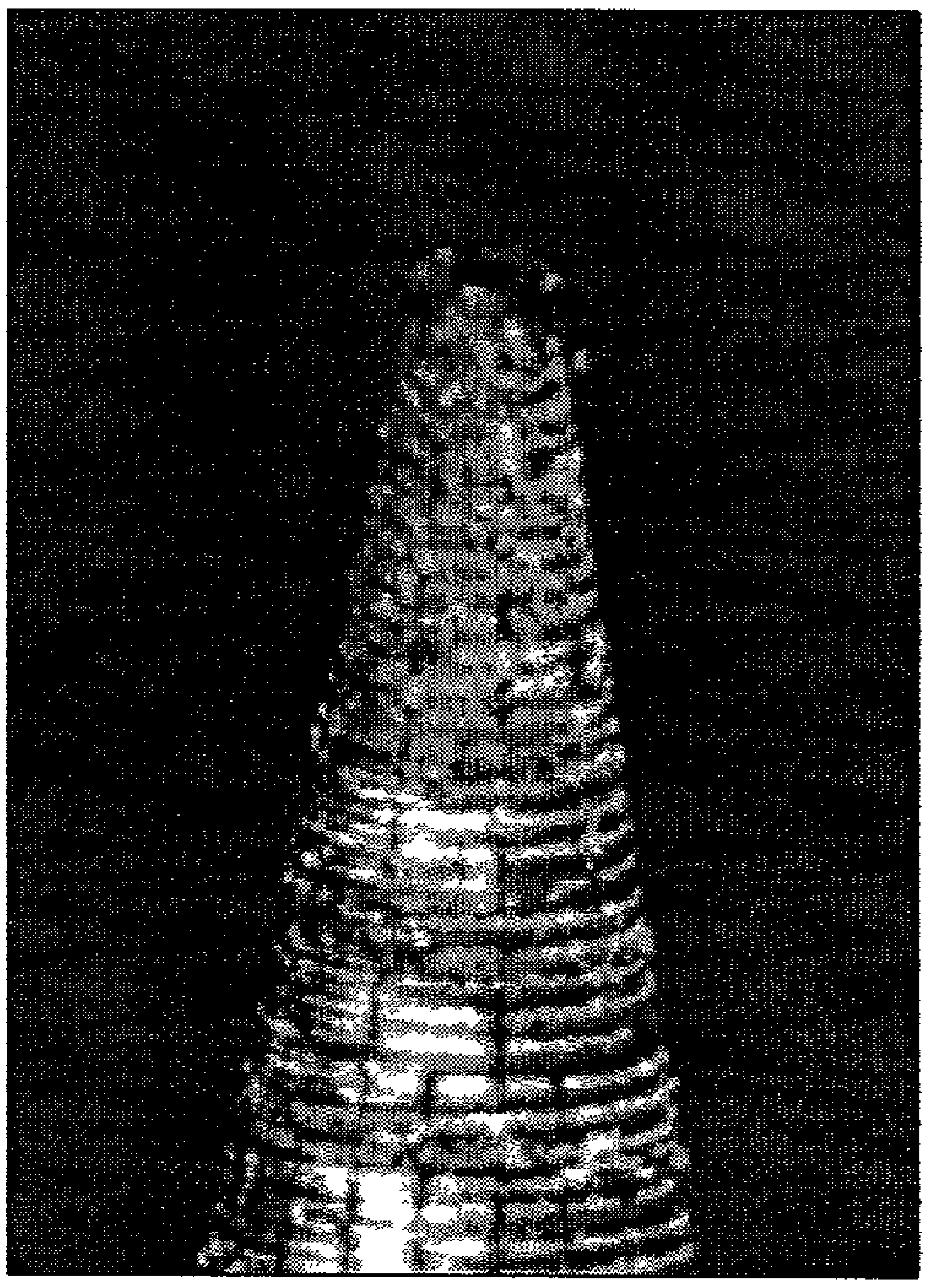

Fig. 11

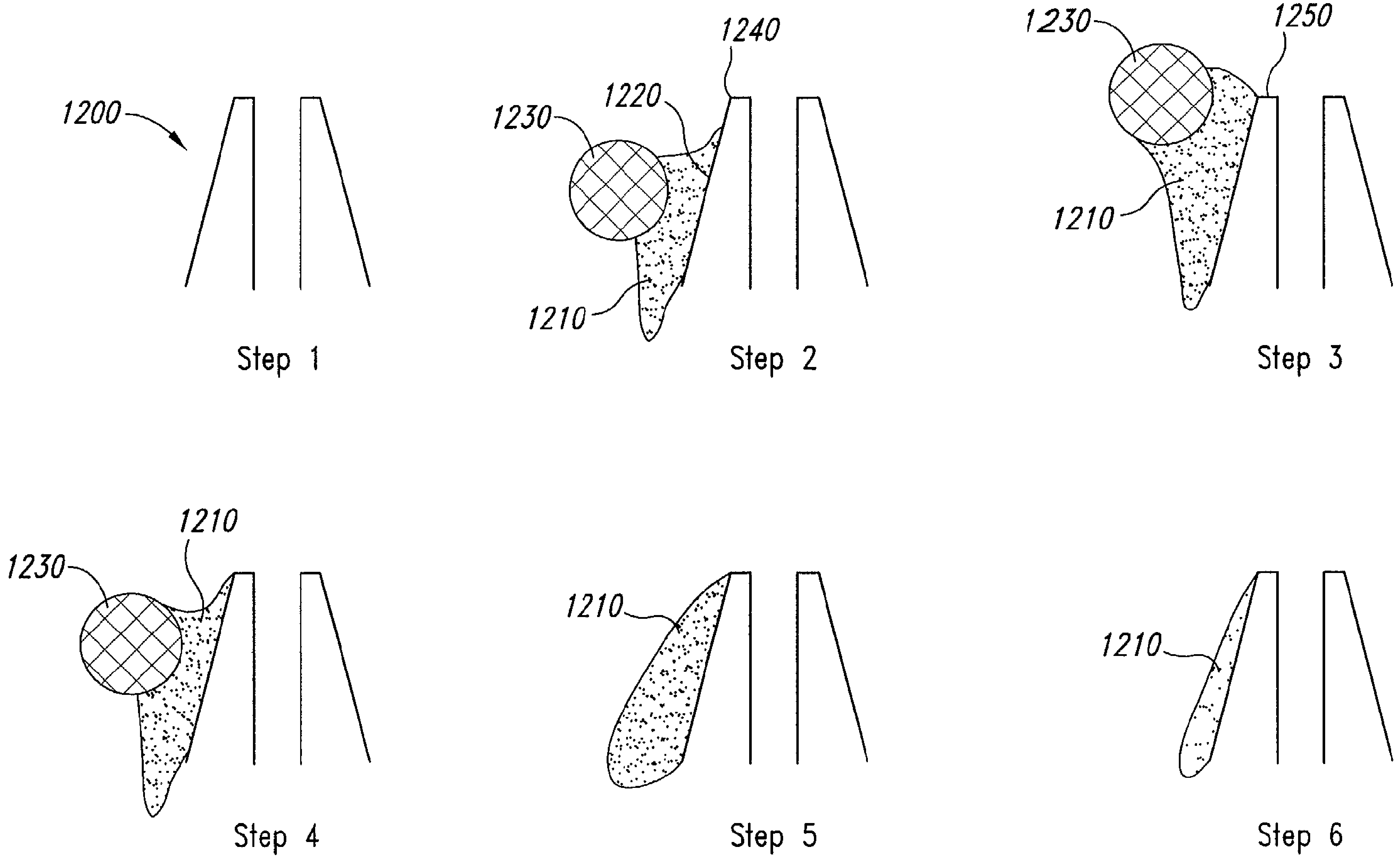
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Fig. 12

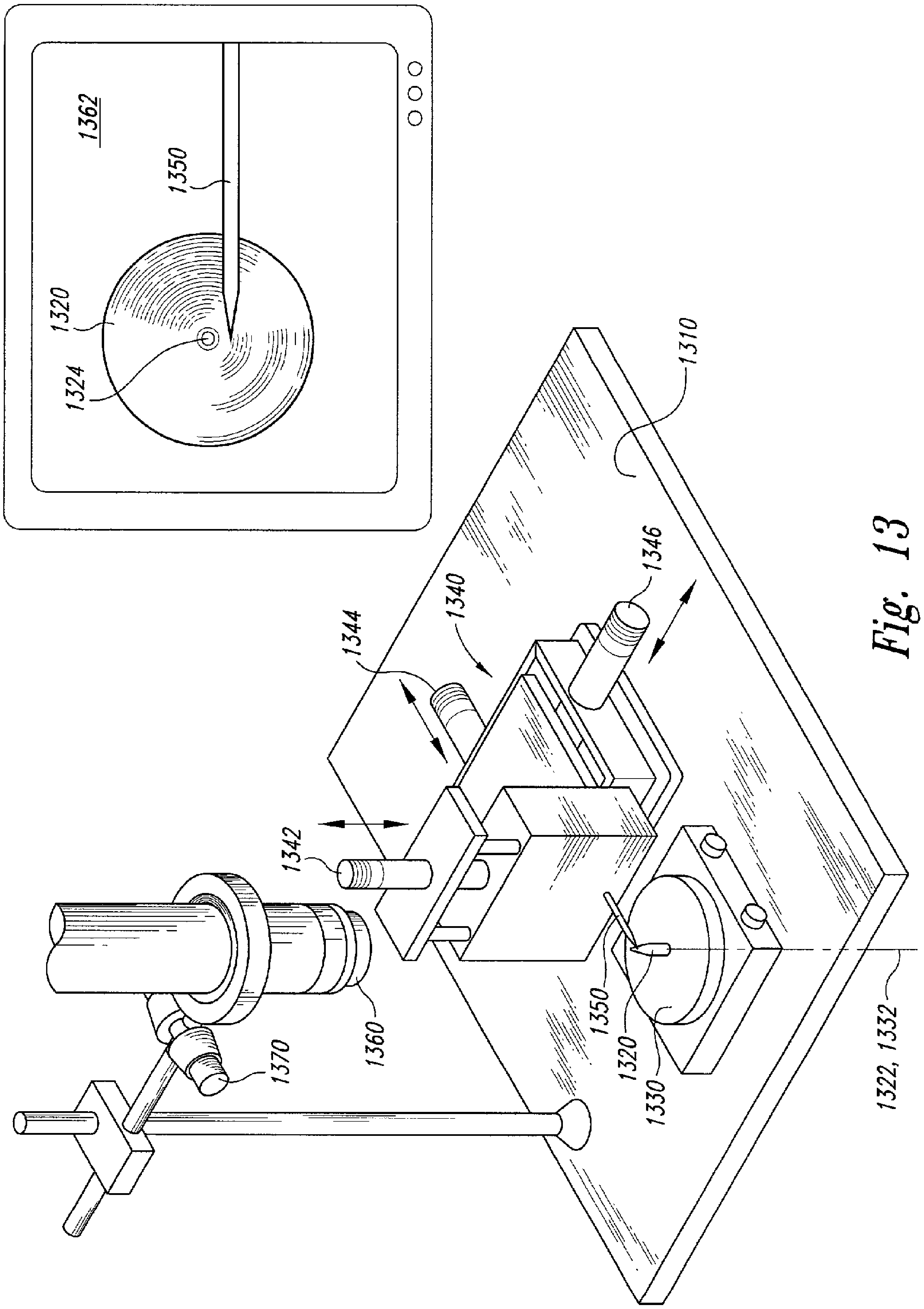
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Fig. 13

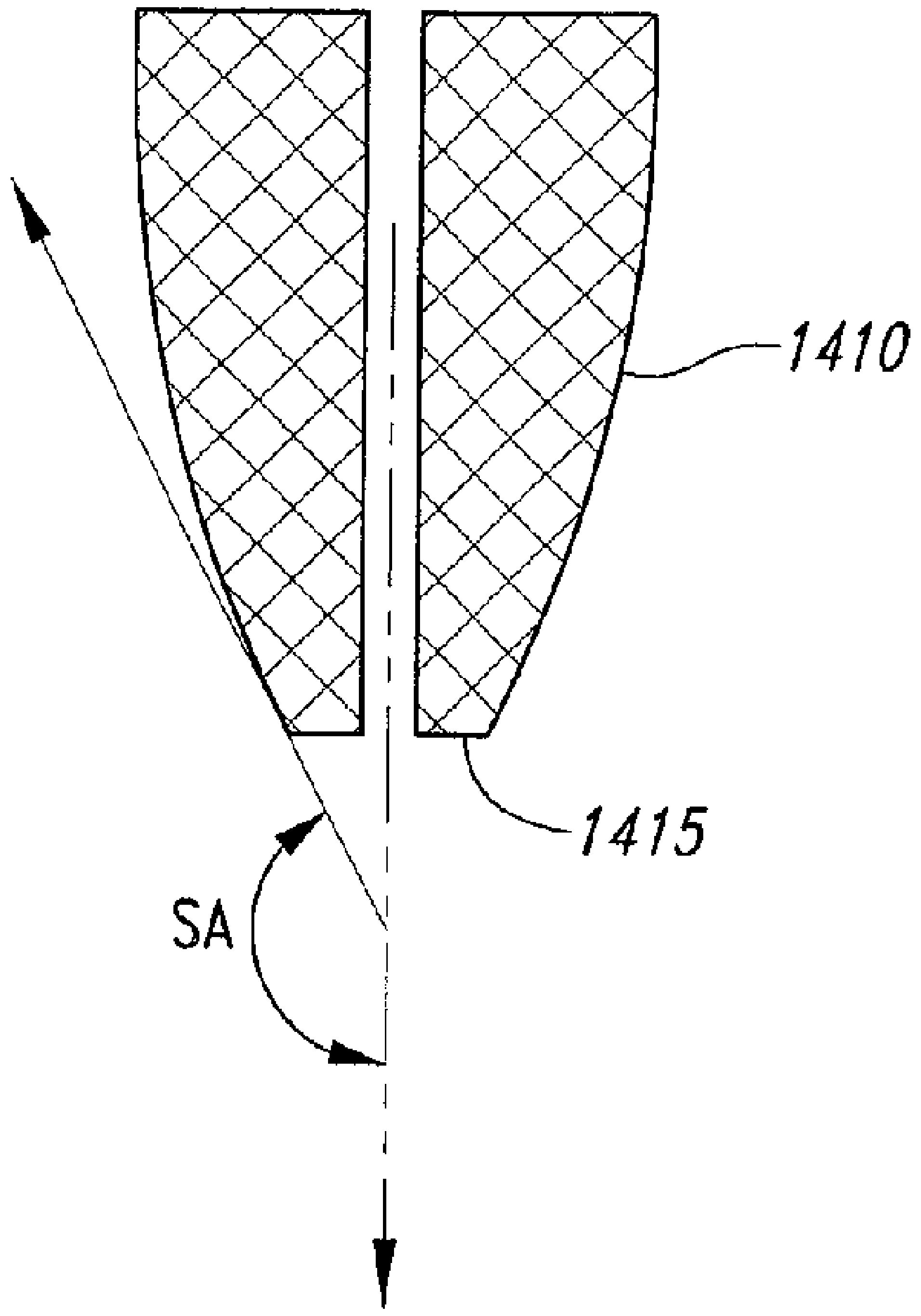

Fig. 14A

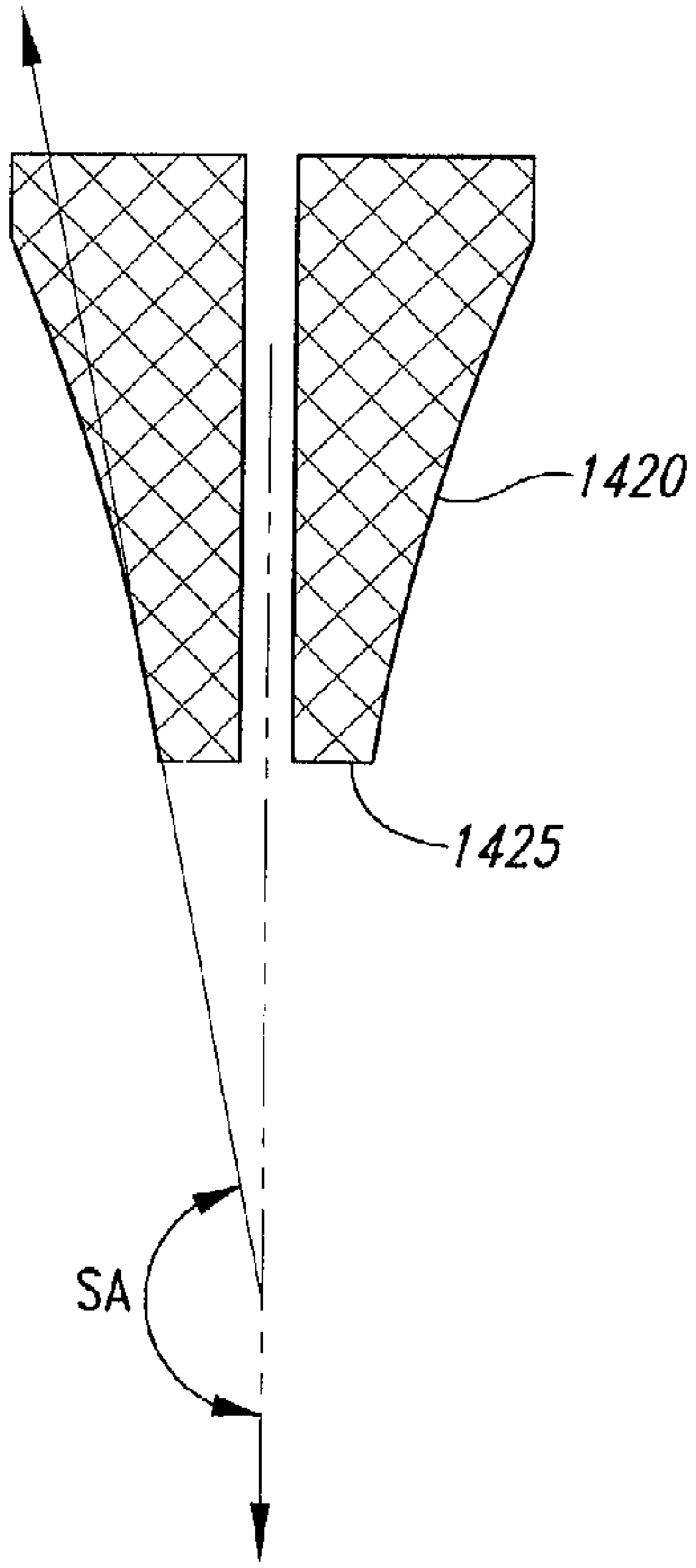

Fig. 14B

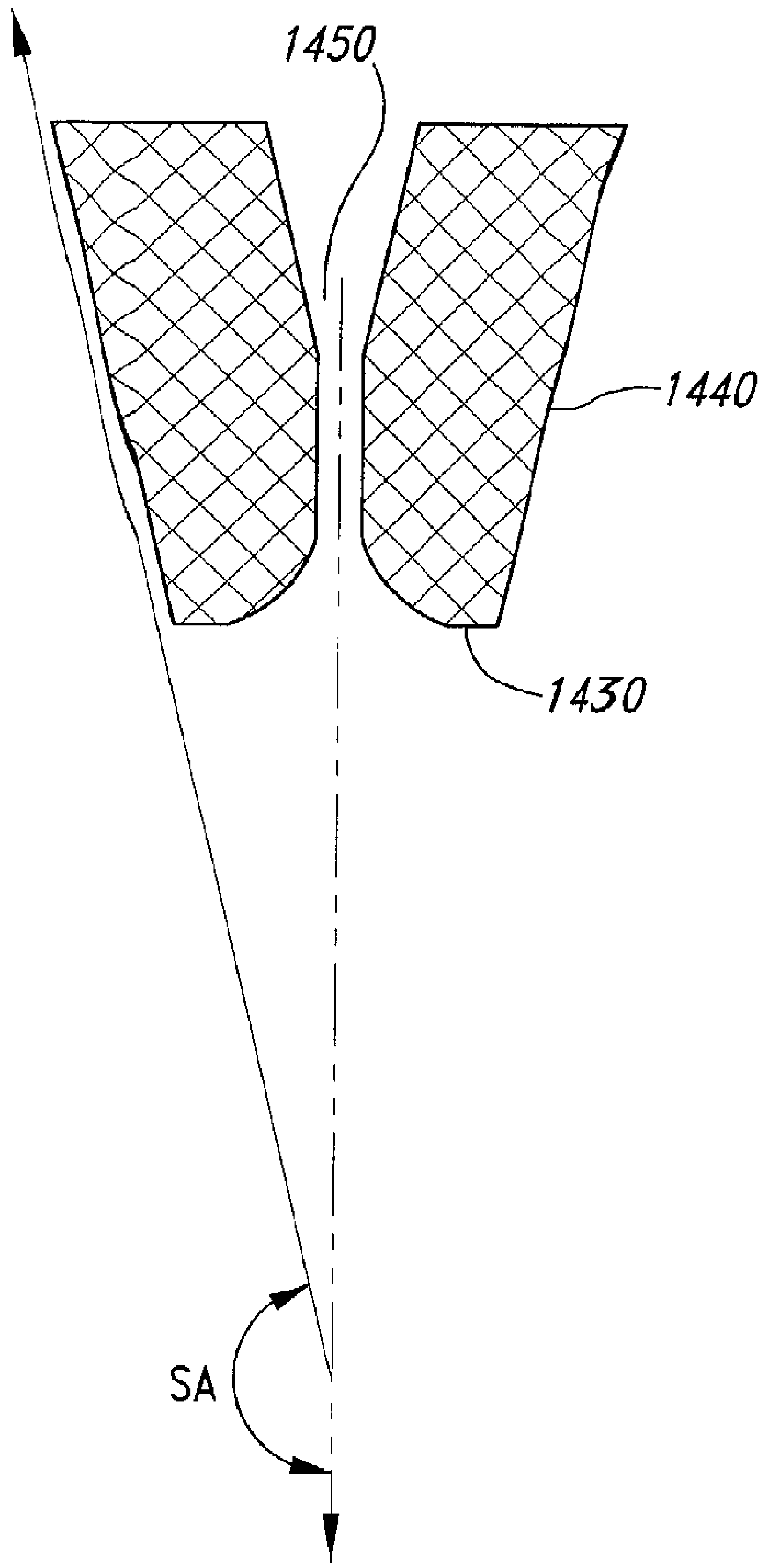

Fig. 14C

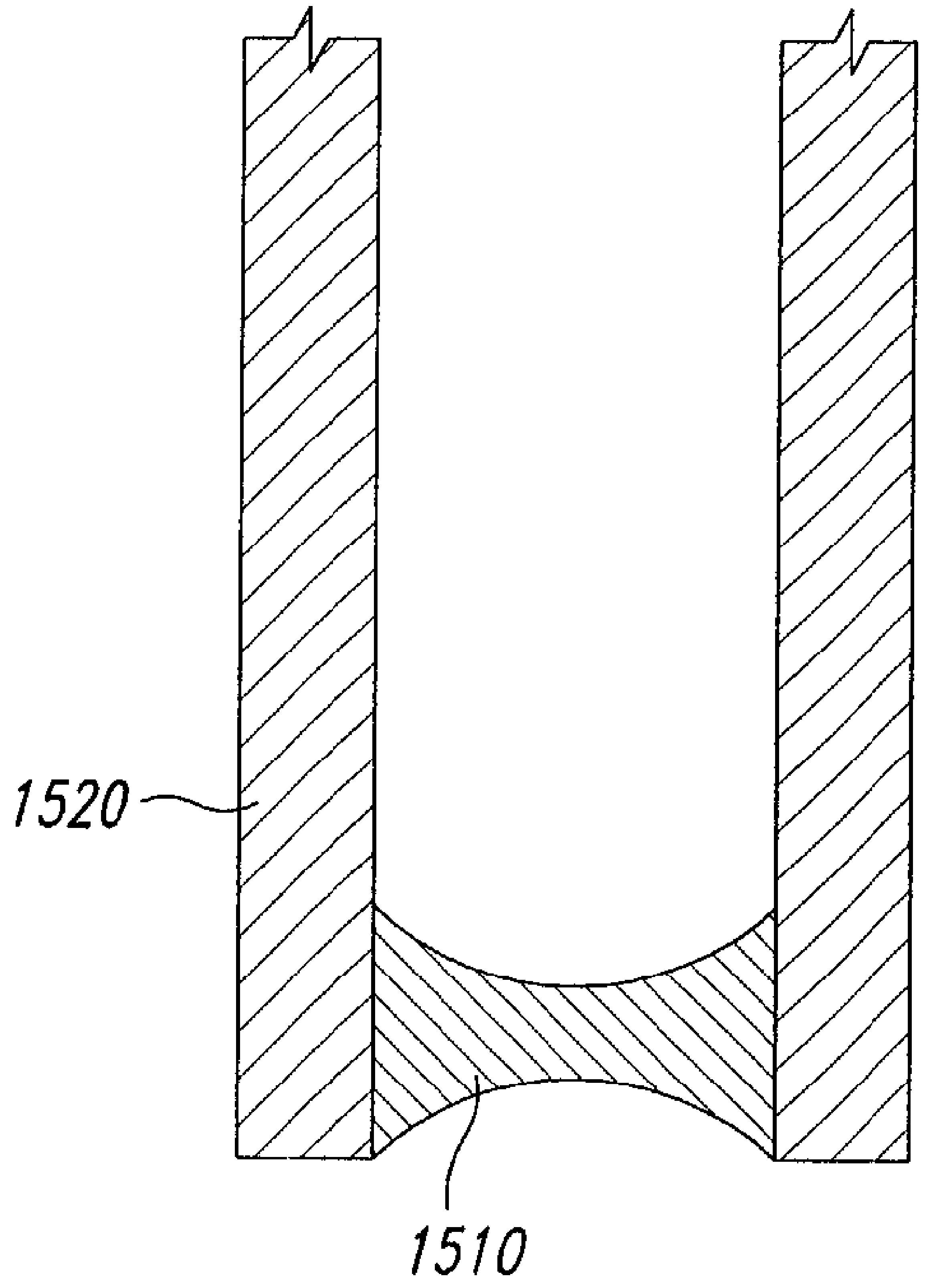

Fig. 15A

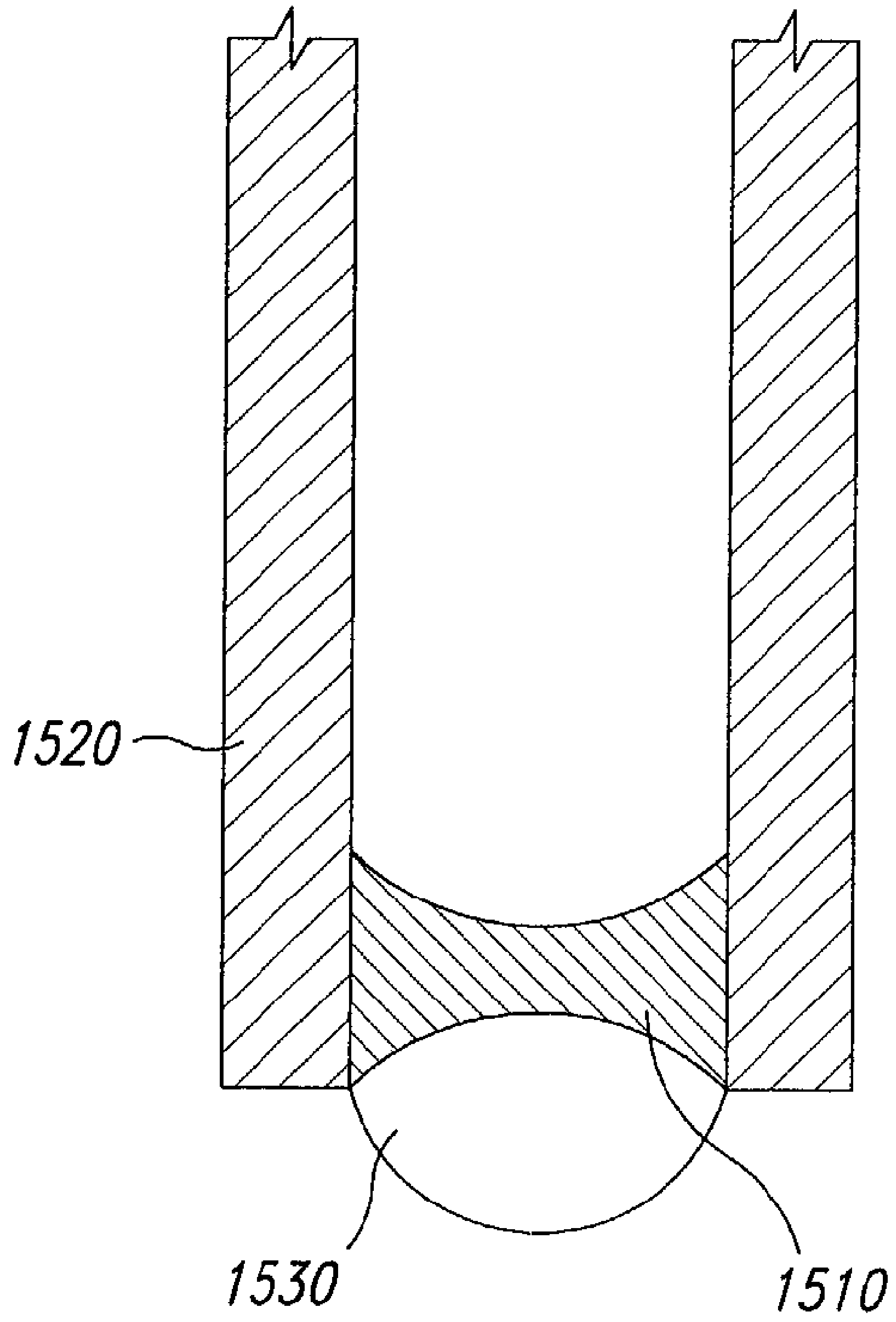

Fig. 15B

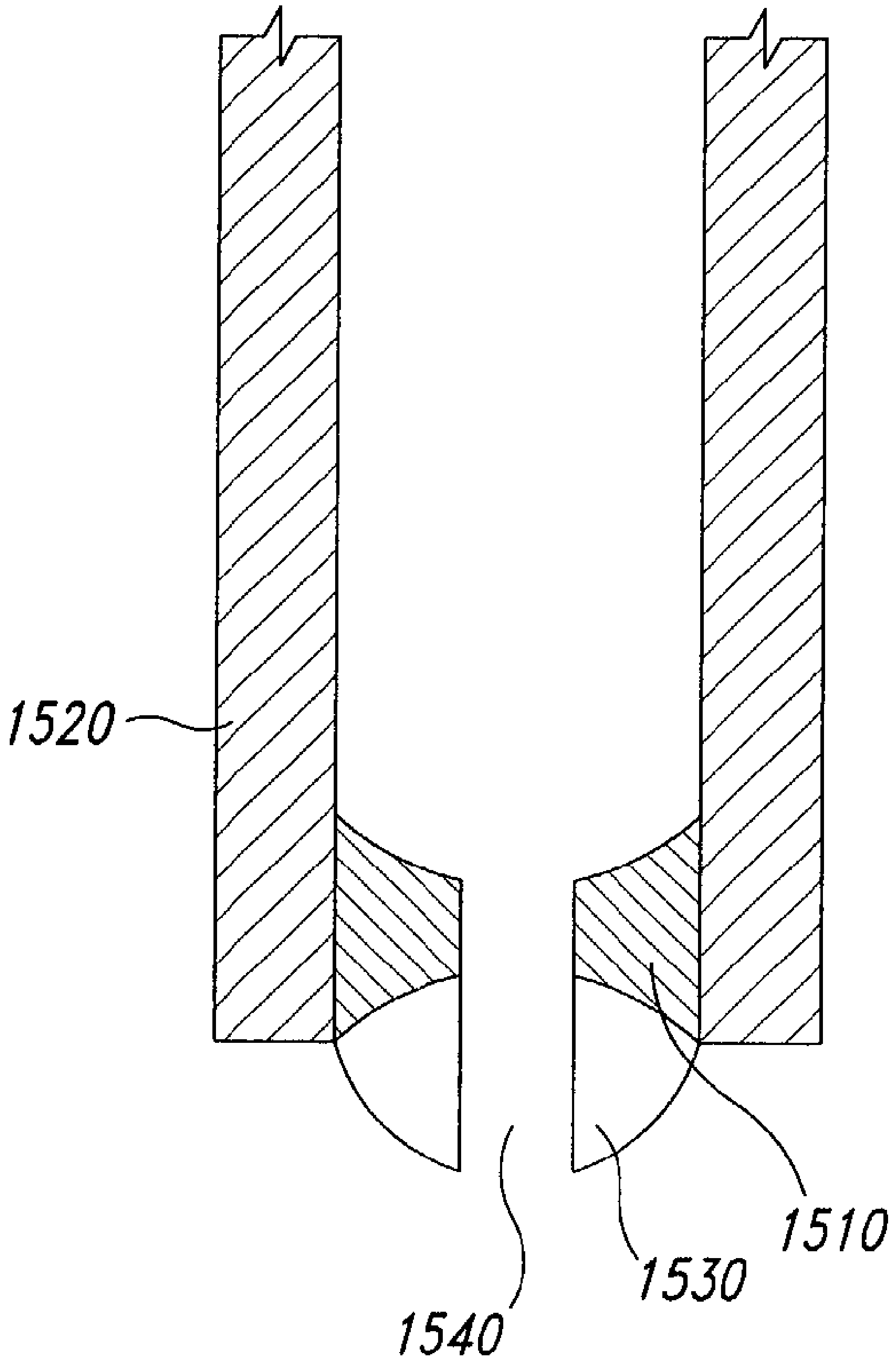

Fig. 15C

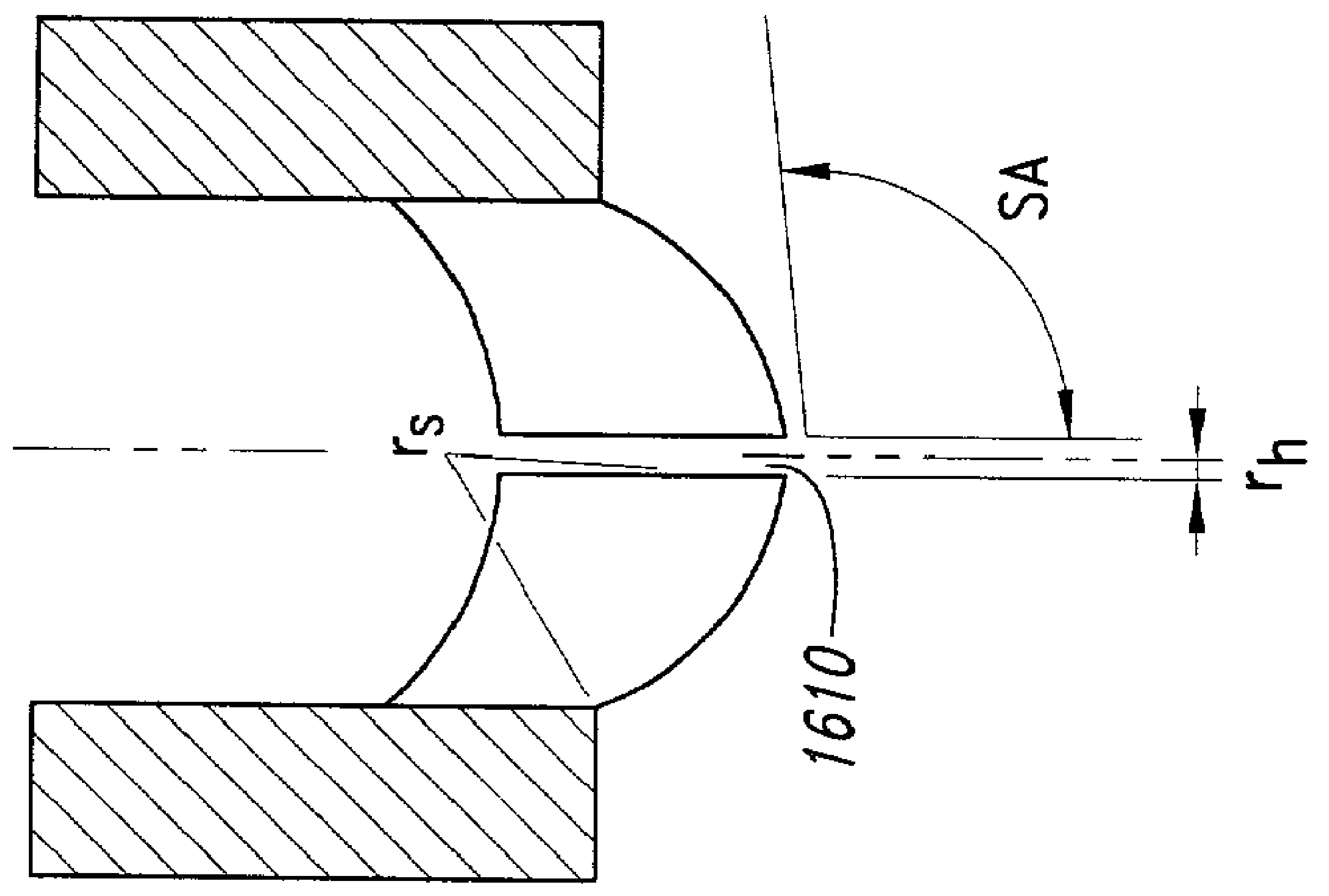

Fig. 16A

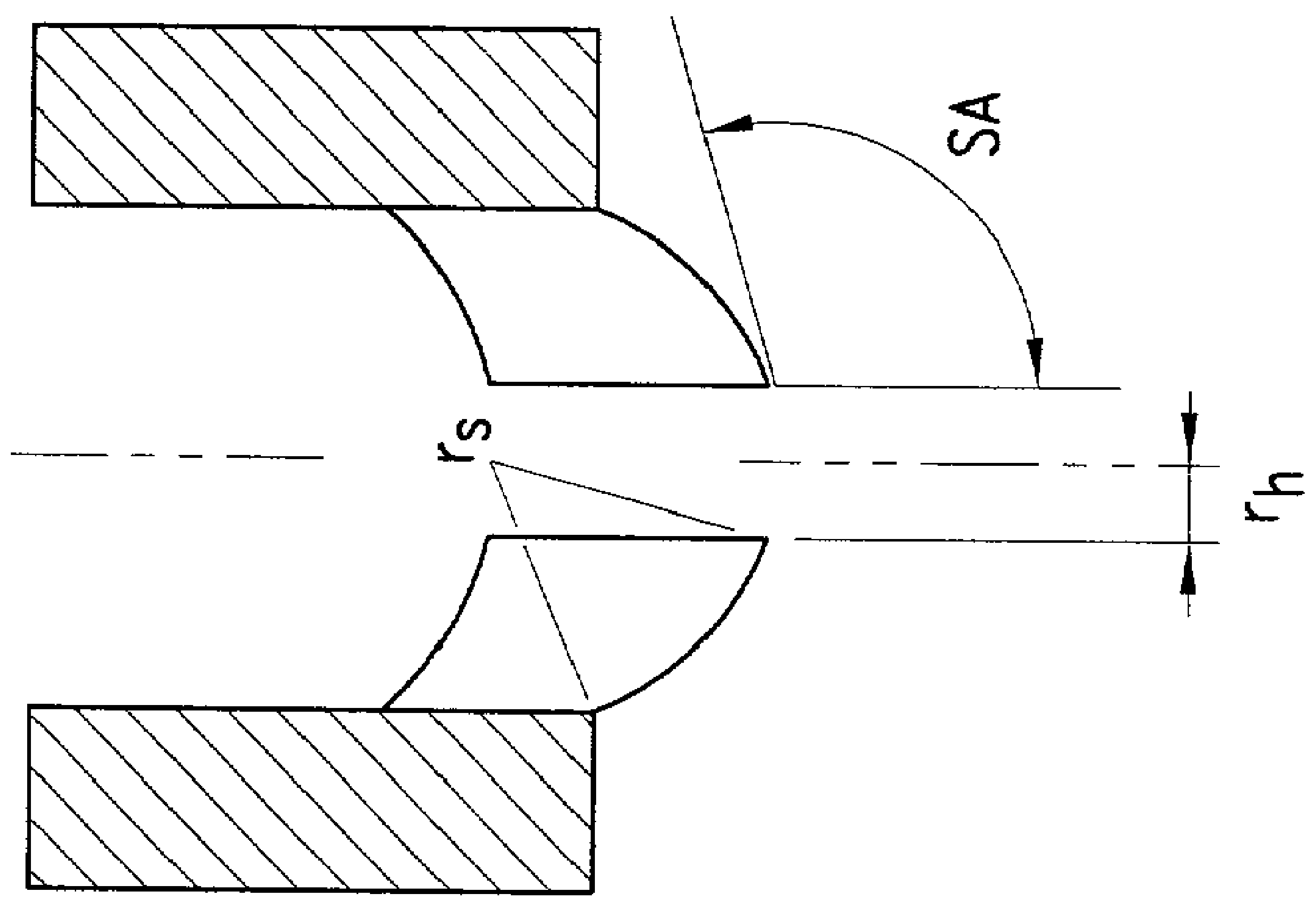

Fig. 16B

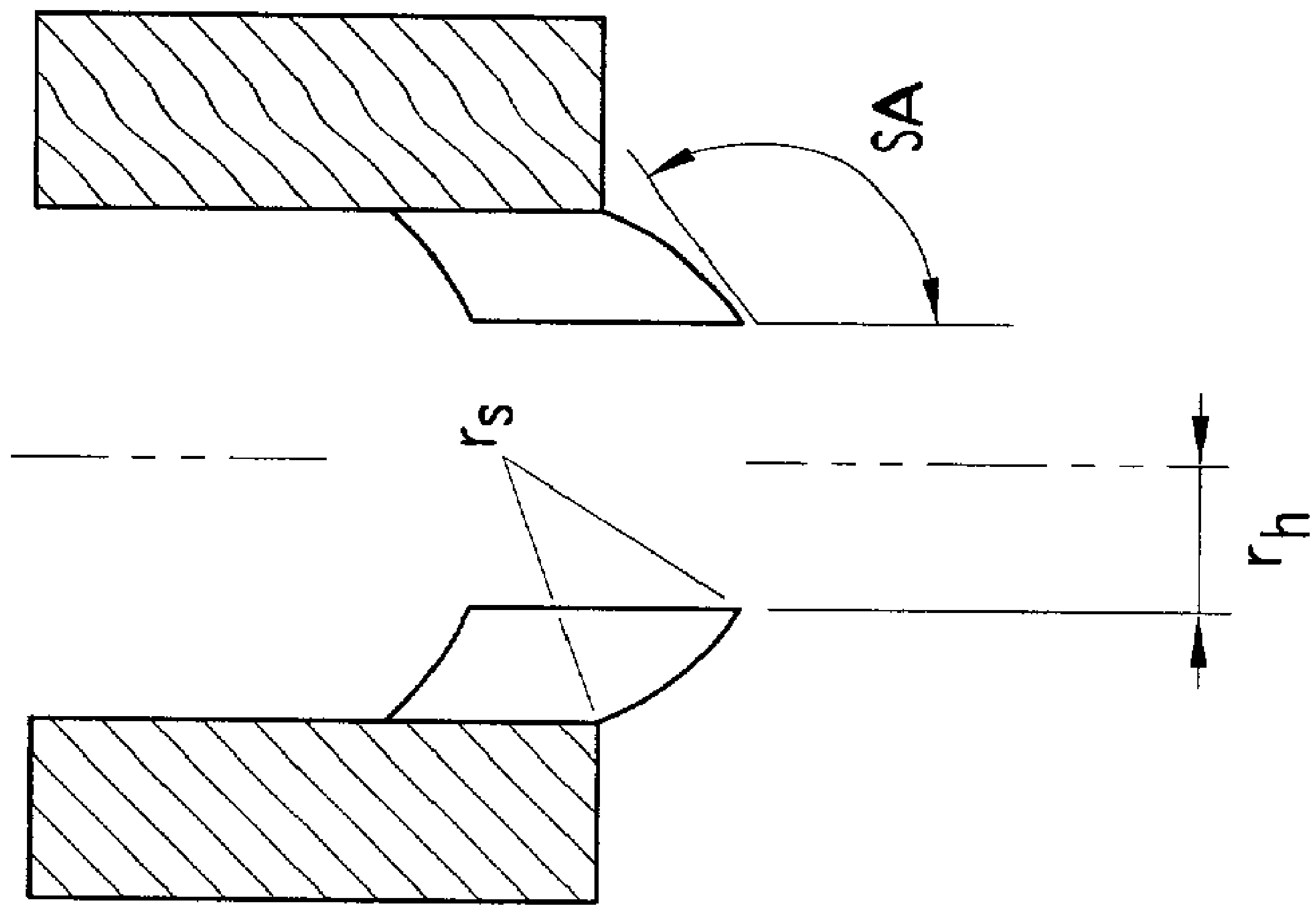

Fig. 16C

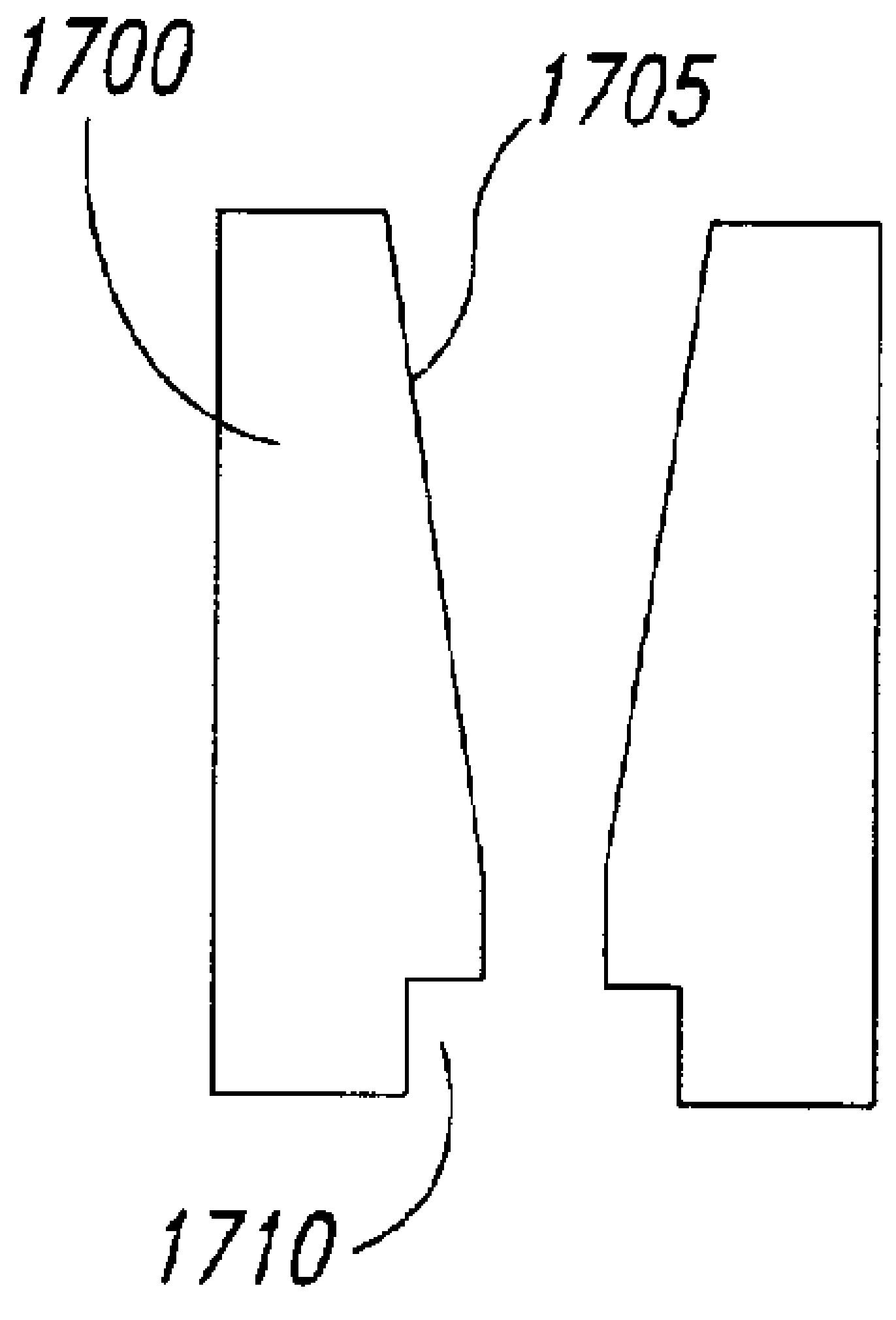

Fig. 17A

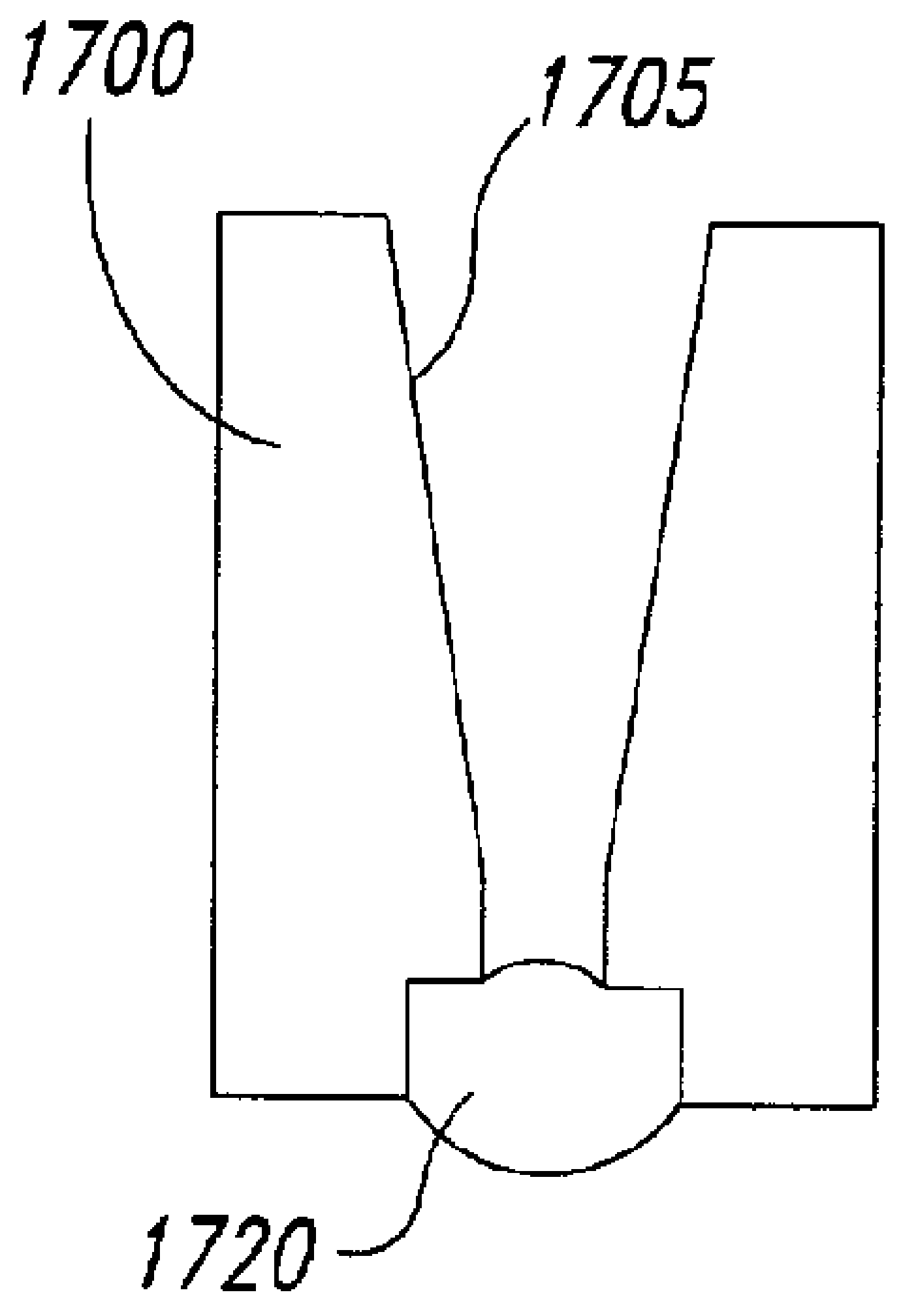

Fig. 17B

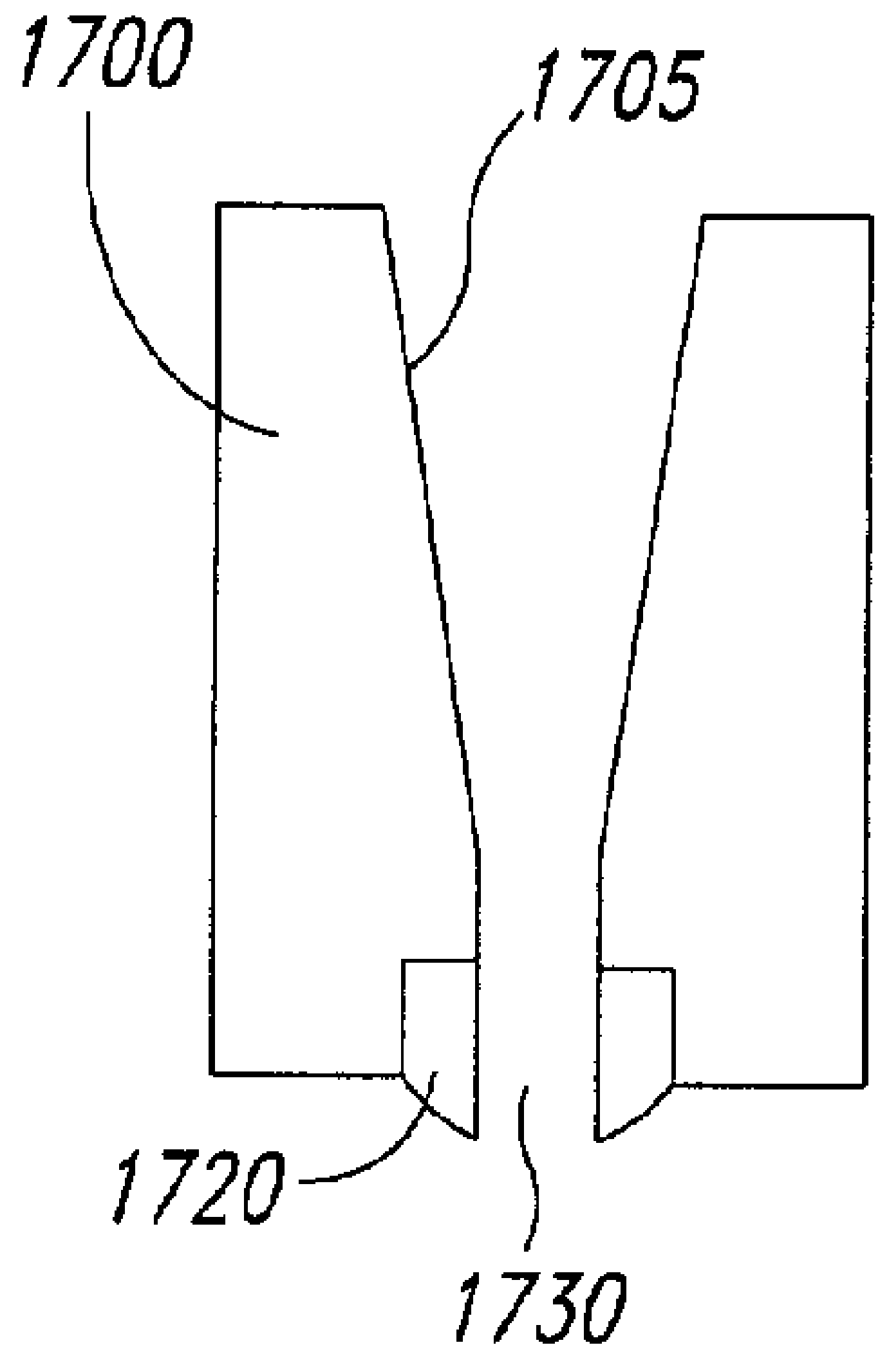

Fig. 17C

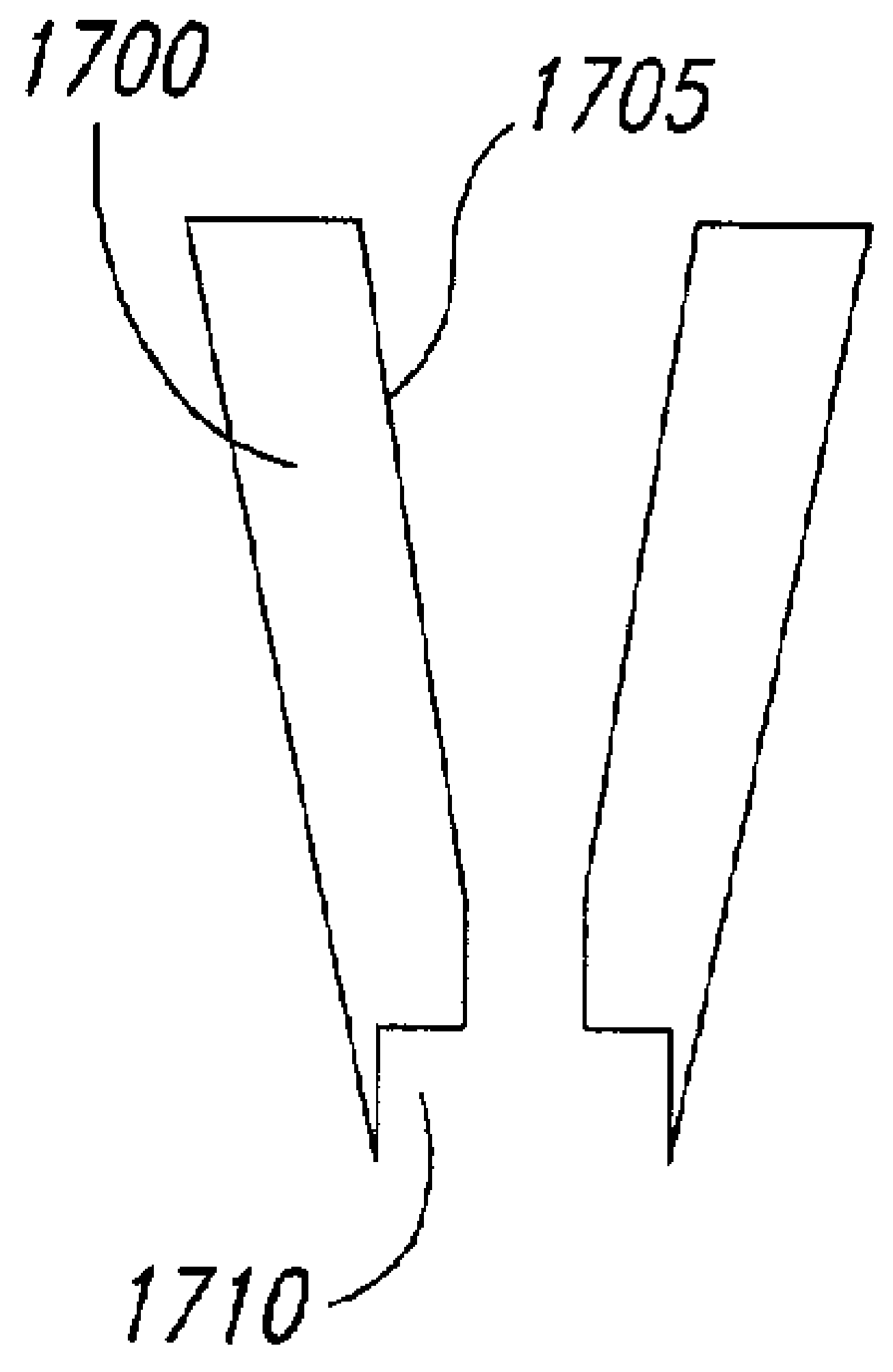

Fig. 17D

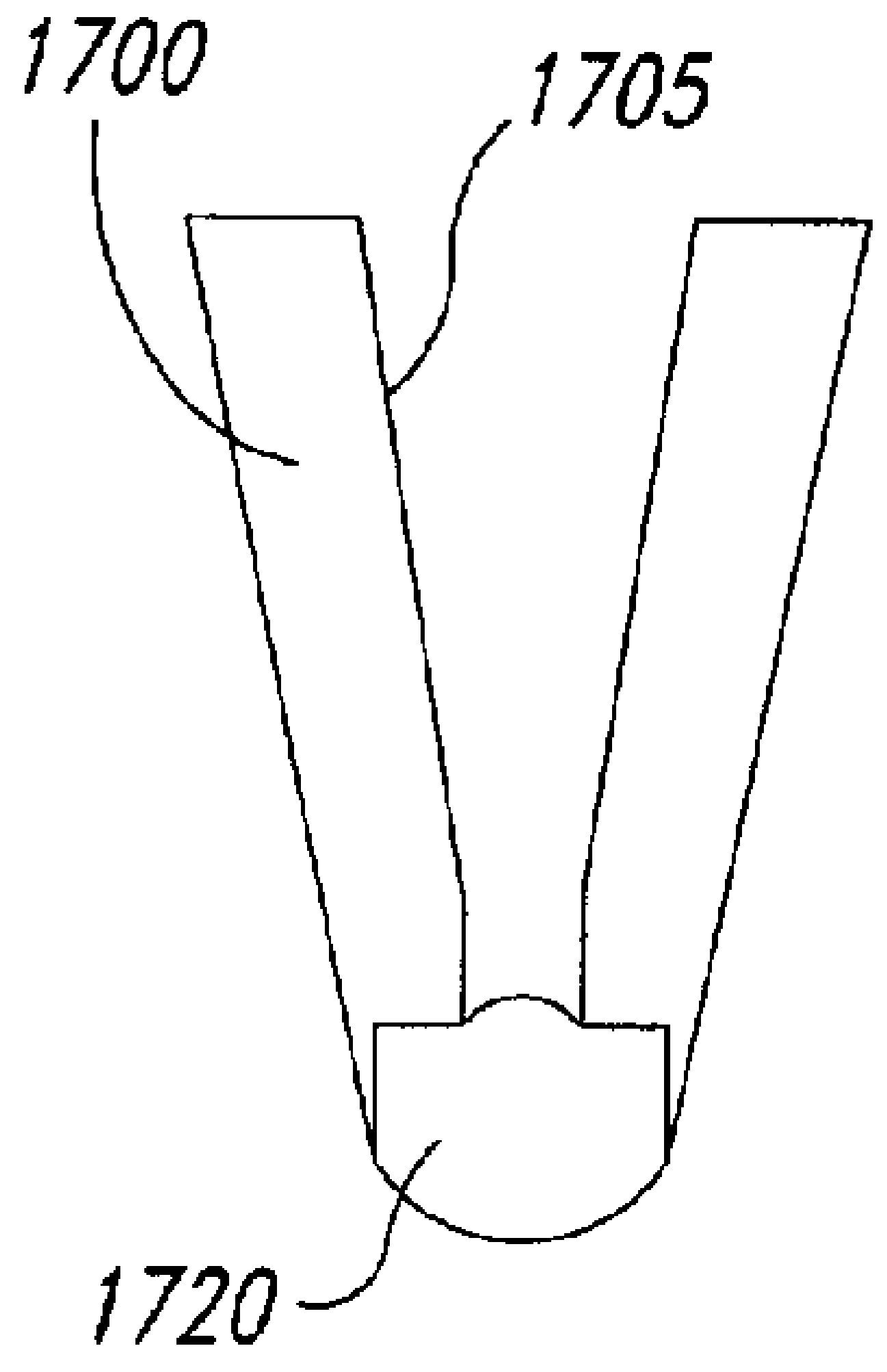

Fig. 17E

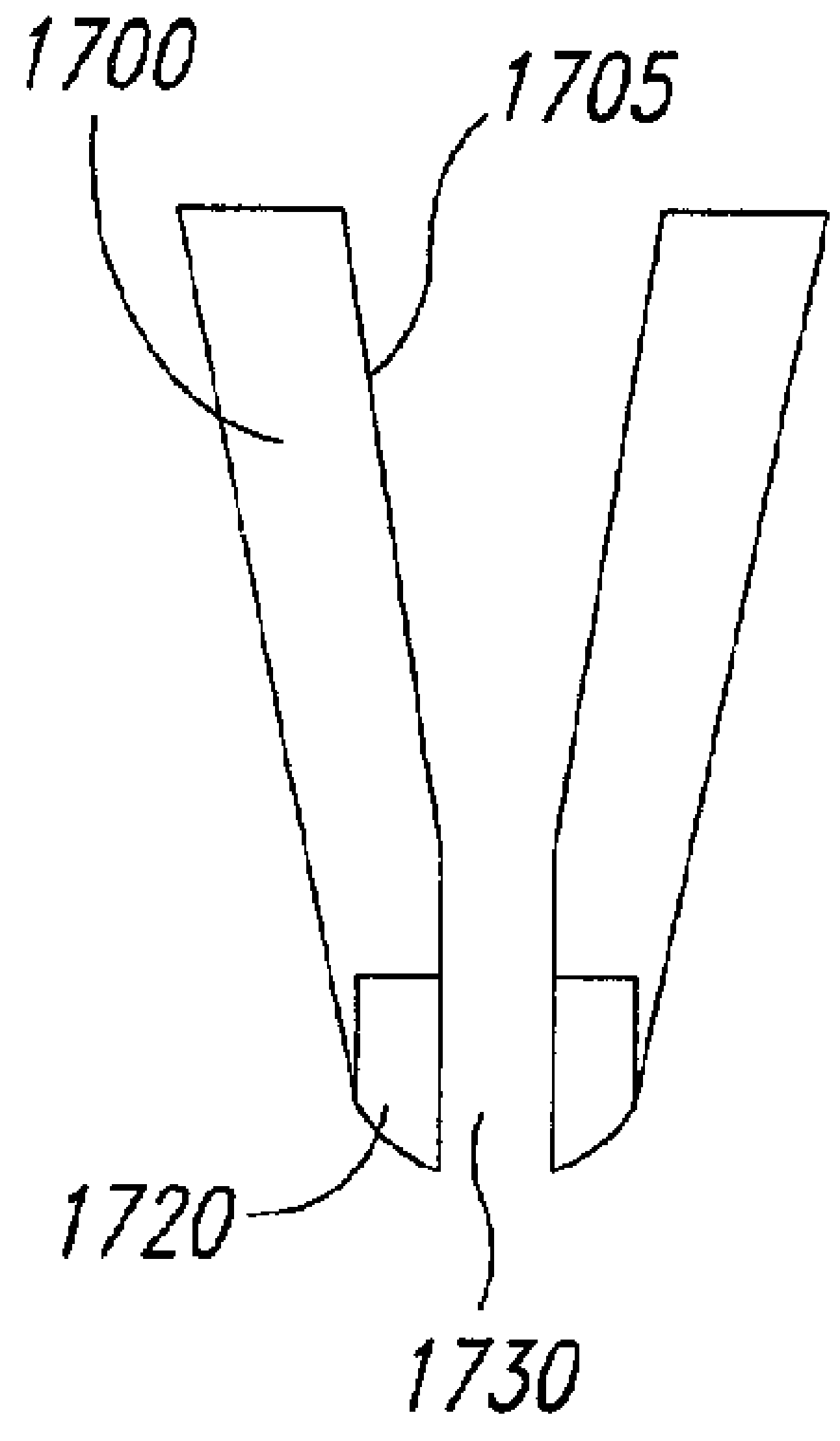

Fig. 17F

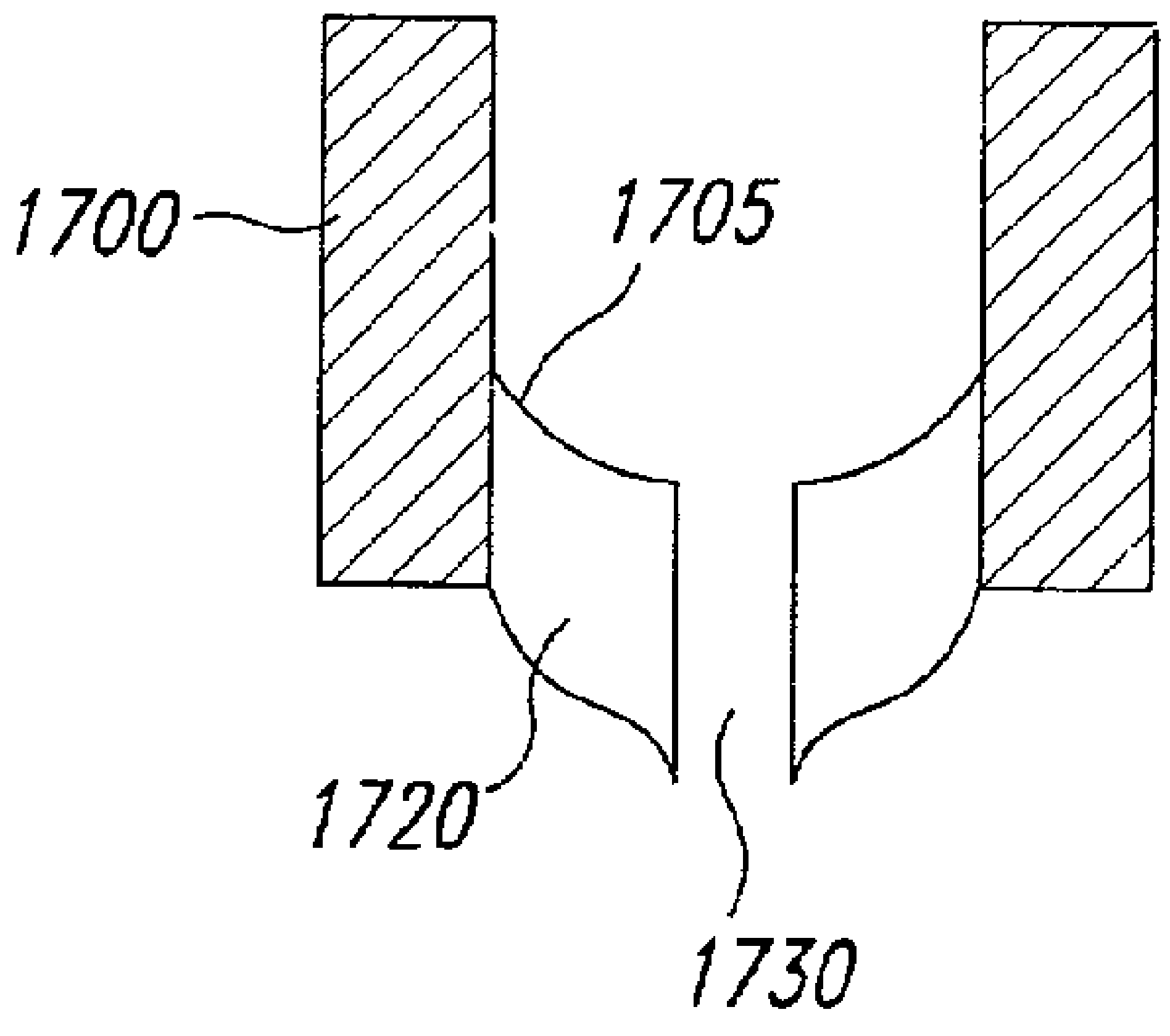

Fig. 17G

METHOD AND APPARATUS FOR DISPENSING SMALL VOLUME OF LIQUID, SUCH AS WITH A WETING-RESISTANT NOZZLE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of Provisional Application No. 60/247,176, filed on Nov. 10, 2000, and Provisional Application No. 60/284,783, filed Apr.18, 2001, and Provisional Application No. 60/288,025, filed May 1, 2001, each of which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] This invention relates to dispensing liquids in small volume droplets or narrow diameter jets, and more particularly, to a wetting-resistant nozzle capable of dispensing small volume droplets or narrow diameter jets, wherein the nozzle has a low surface energy coating and/or a nozzle geometry to provide wetting resistance.

[0004] 2. Description of the Related Art

[0005] Dispensing liquids is important in various technologies. Ink-jet printing is a major application involving the precise dispensing of tiny drops. Another application is three-dimensional printing (3DP), in which layers of powder are bound together in by precisely dispensed binder liquid to form three-dimensional objects. Yet another application is dispensing of pharmaceuticals and other liquids for manufacturing medical devices and dosage forms.

[0006] Dispensing small volume droplets to create printed displays, pharmaceuticals, medical devices and the like, requires precise, predetermined quantities of liquid delivered in precise, predetermined locations. One problem currently encountered in dispensing small volume droplets has been the uncontrolled and inconsistent degree to which the dispensed liquid wets or does not wet the exterior surface of the nozzle. Wetting is undesirable for precision dispensing of liquids because it is a randomizing influence. Ideally, liquid that passes through the passageway of the nozzle should be ejected toward the target as soon as it is dispensed, in a predetermined quantity and directed to a specific location. However, if wetting occurs, a puddle forms at the nozzle exit, and when the liquid from the dispenser enters the puddle it may or may not immediately exit the puddle because the puddle has variable volume. Some or even all of the liquid may go to changing the size of the puddle rather than being dispensed. Most or all of the puddle will eventually be ejected as a very large drop, which is especially undesirable.

[0007] In addition to introducing a randomizing influence on the quantitative dispensing of a liquid, wetting or the presence of a puddle can effect the direction of dispensed liquid. Misdirection is a change in the angle of the stream, so that the direction of the stream's travel after leaving the nozzle is different from the direction of the passageway through the nozzle. Split-streaming occurs when the liquid dispenses as two distinct streams virtually simultaneously. These effects are undesirable in drop-on-demand applications, in which each drop is dispensed by directed action of the valve or dispenser, as well as other forms of dispensing. Another undesirable effect that can also occur is called swingback and is described later.

[0008] Typical ink-jet ink has a surface tension of 33 dyne/cm and a viscosity of 8 centiPoise (at room temperature), while water has a surface tension at room temperature of 73 dyne/cm. Achieving non-wetting dispensing becomes increasingly more difficult when dispensing ink below the mid-30's for surface tension of the liquid. Current ink-jet printing technology uses nozzles with various coatings and designs to print liquids with surface tensions down to the 30's of dyne/cm.

[0009] With traditional ink printing, the ink has been designed to meet the limitations of the nozzle. For example, for a given nozzle design, the composition of the ink will be engineered and modified with additives to achieve the performance characteristics required to print with a given nozzle. Thus, ink compositions are engineered to keep surface tension and viscosity above certain minimum values, namely, 30's of dyne/cm. Commercial ink-jet developers have thus avoided designing nozzles for the region of fluid properties that have surface tensions below 30 dyne/cm by developing aqueous based inks that are elaborately engineered with combinations of additives.

[0010] Organic solvents have thus been particularly difficult to dispense. Organic solvents may have both low surface tension and low viscosity. The organic solvents of greatest practical interest have surface tensions in the 20's dyne/cm and viscosity around or less than 1 cP. Their low surface tension makes the liquid want to wet or form a puddle at the nozzle exit, and inhibits droplet break off. The viscosity of the liquid helps to pull liquid off of the exit region, overcoming surface tension and forming drops. If the viscosity is low, the fluid stream may not break into droplets, but instead may stretch and display related problems. This combination makes organic solvents more likely than water to wet the nozzle during dispensing. Organic solvent are important in manufacturing medical products by 3DP because some substances of medical interest are soluble only in such solvents, not in water.

[0011] One consideration in controlling wetting behavior is the geometric design of the nozzle. The simplest possible nozzle design is a simple orifice, for example, a hole through a large flat surface. Such nozzles are commonly used in applications such as waterjet cutting and are typically made of sapphire or ruby with a hole drilled through a flat exit surface. These orifices are only available with a flat exit surface or with a recessed exit. The jewel is typically held in the end of a tube of outside diameter such as 0.050-inch whose edge is typically crimped over the edge of the jewel. In applications involving dispensing of drops, such nozzles are prone to wetting because of the flat exit geometry and the fact that the jewel is not a particularly low-surface-energy material.

[0012] **FIG. 1** illustrates unsatisfactory nozzle performance of a flat exit surface nozzle **100**. As shown, a puddle **120** much larger than the dispensed drop **130** forms at the flat exit surface **110**. Especially with organic solvents, such an orifice suffers significantly from wetting with the establishment of an ongoing puddle that contributes to inconsistent dispensing of the drops. Thus, such flat exit surface nozzles are not optimal for precision fluid dispensing, especially of organic solvents.

[**0013**] Another nozzle currently in use has a sharply tapered cone having typically 30 degrees total included angle; an internal passageway with a gradual transition of cross-sectional area inside the body of the nozzle, being narrowest at the tip of the nozzle; and a filleted transition region between the internal passageway and the external surface. These nozzles have been typically made for use as wire-bonding tools in the microelectronics industry; thus, the design is not optimal for limiting the spread of the liquid when printing.

[**0014**] Some other commercially available nozzles have been made with a flat end (land), and are intended for use as vacuum pick-up tools. Materials from which they are commercially manufactured include tungsten carbide, Delrin™ (an acetal polymer), and alumina (aluminum oxide). In such nozzle geometry, particularly the vacuum pick-up tools that are flat-ended, the much-reduced size of tip together with its sharp edges can help limit the size of the puddle that may form. However, such geometry can exhibit another problem, namely, swingback. Swingback is illustrated in FIGS. **2**A-**2**C.

[**0015**] FIGS. **2**A-**2**C are illustrations of dispensed liquid from a commercially available nozzle illustrated as still frames of video taken at a capture rate of 30 frames per second. The nozzle illustrated in FIGS. **2**A-**2**C were made of Delrin™ an acetal polymer. The liquid being dispensed was a solution of 40% ethanol, 60% water, and has surface tension and viscosity closer to the properties of pure ethanol than to the properties of pure water. The inside diameter of the nozzle orifice was 0.006 inch (152 microns). The exit geometry was a flat cutoff (sharp-edged) as in a vacuum pick-up tool, with the outside diameter of the land (flat region) measuring 0.010 inch (254 microns). After the small flat land, the nozzle exterior sloped back with a total included angle of 30 degrees (15 degree half-angle). The direction of dispensing was vertically downward.

[**0016**] In **FIG. 2**A, the stream of liquid **210** is dispensing from the nozzle **220** and the exterior conical surface **205** of the nozzle **220** is dry. In **FIG. 2**B, the stream of fluid **210** has shut off and a drop of liquid **230** has swung up onto the conical exterior **205** of the nozzle **220**. **FIG. 2C** illustrates that the swung-back drop of liquid **230** pulls a subsequent stream of fluid off-axis.

[**0017**] If this sequence is repeated, the swung-back drop on the external conical surface can grow with incorporation of additional liquid at each shutoff. The swung-back drop is a source of asymmetry on an otherwise symmetrical nozzle and it interferes with precise dispensing by causing misdirection and/or split-streaming. Additionally, the swung-back drop detaches randomly as a dispensed large drop.

[**0018**] Dispensed liquid exits the nozzle and moves downward due to both gravity and momentum from the pressure-driven flow. Liquid has to move upward in opposition of both the direction of gravity and the direction of the dispensed momentum in order for swingback to occur. The dominant physical mechanism causing swingback is the surface tension of the liquid.

[**0019**] Similar nozzles made of tungsten carbide with flat ends were tested and also exhibited results that were unsatisfactory and in some cases, the results were worse. Similar nozzles of polished alumina but with fillets also exhibited unsatisfactory performance. Polished alumina is believed to be slightly better than Delrin™ as far as surface energy, while the geometry involving fillets is believed to be slightly less favorable than the sharp-edged geometry. The filleted geometry is manufactured because it is useful for wire-bond tools and with alumina it is not possible to manufacture sharp-edged nozzles. Thus, even though all of these nozzles have a small-tip externally tapered geometry that can be expected to be more advantageous than the nozzle of **FIG. 1**, when used with organic solvents they still suffer from wetting or swingback.

[**0020**] Extensive testing has shown that with many of the organic solvents of interest, the nozzles made from all of these commercially available materials still suffer wetting of the outside cone, and in particular suffer swingback of the last little bit of liquid upon shutoff.

[**0021**] The literature contains a variety of materials and coatings that have been developed to attain low surface energy and good non-wetting characteristics. A convenient reference point is the well-known material Teflon™ (polytetrafluoroethylene), which has a surface energy variously quoted as 18-22 dyne/cm, most frequently 18 dyne/cm, and has a contact angle with water of 100 degrees. Of materials that are widely known and available, Teflon is perhaps the most hydrophobic.

[**0022**] In Physical Chemistry of Surfaces by Arthur W. Adamson and Alice P. Gast (John Wiley, New York, 1997) p. 356, referencing E. G. Shafrin and W. A. Zisman, J. Phys. Chem., 64, 519 (1960), there is a chart summarizing hydrophobic polymers by chemical family and by the particular atomic constitution at the surface. Of the chemical families in that chart, fluoropolymers are in general the most hydrophobic. The surface constitution $—CF_2—$, is listed on that chart with a surface energy of 18 dyne/cm and is described as representing Teflon™ (polytetrafluoroethylene and related substances). Teflon has a sufficiently low surface energy that nozzles made of it alone can perform reasonably well with aqueous solutions. However, even Teflon is not of sufficiently low surface energy to perform satisfactorily with most organic solvents.

[**0023**] In the same chart, the chemical radical with the lowest surface energy is the terminal trifluoromethyl group $—CF_3$. Zisman concludes that the best surface constitution for non-wetting is terminal trifluoromethyl groups ($—CF_3$). The radical which is terminal $—CF_2H$ groups is not as hydrophobic as terminal trifluoromethyl groups but is marginally better than the $—CF_2—$ groups which describe Teflon.

[**0024**] A family of especially low surface energy materials is available from the Cytonix Corporation, Beltsville, Md. The materials are described in U.S. Pat. Nos. 5,853,894 and 6,037,168. These substances are characterized by having a terminal trifluoromethyl group, and in particular by having the exposed surface contain a high fraction of these terminal trifluoromethyl groups. These are believed to be essentially the lowest surface energy materials known. It is possible to achieve surface energies as low as 10 or even 6 dyne/cm. The most hydrophobic properties are achieved when the coating has an exposed surface consisting almost entirely of trifluoromethyl ($—CF_3$) groups, that is, 100% of the area, with no other substituent groups exposed at the surface.

[**0025**] Other nonwetting substances are also listed in these patents. In particular, for these materials, it is found that the surface energy is lowest on the surface that is exposed to the atmosphere while curing or drying. At surfaces which were not created during the curing or drying process but rather were exposed later such as by a machining or cutting operation, the surface energy is not so low, i.e., the material is not so hydrophobic. Under best conditions, the surface energy achievable with these fluoropolymers at the cured surface is 6 to 12 dyne/cm. Expressed in terms of contact angle, these substances have reached contact angles for water as high as 150 degrees. There are various formulations including highly fluorinated epoxy (fluoroepoxy), polymer which is heat-curable or curable by exposure to ultraviolet light with the curing causing polymerization, polymer which is already polymerized and dissolved in a fluorosolvent, resins of varying viscosities, etc.

[0026] Other substances have also been investigated in the literature. While the materials listed below do not have surface energies as low as that of the Cytonix materials, still they are in most cases more hydrophobic than Teflon. What is listed here is sometimes surface energy or critical surface tension and sometimes, contact angle, whichever is reported in the literature.

[0027] U.S. Pat. Nos. 4,344,993, 4,764,564 and 4,554,325, all titled "Perfluorocarbon based polymeric coatings having low critical surface tensions," disclose substances which are modifications of perfluorocarbon and which have critical surface tension less than approximately 14 to 15 dyne/cm, which is described as being lower than that of pure perfluorocarbon.

[0028] U.S. Pat. No. 5,426,458 describes a coating of poly-p-xylylene, which is available under the trade name Parylene N and is intended for adhesion resistance and corrosion resistance, having a contact angle with water of 110 degrees.

[0029] U.S. Pat. No. 5,073,785 comprises applying a coating of amorphous or diamond-like carbon followed by fluorination of this layer, having a contact angle with water of about 105° (100°±5 degrees). U.S. Pat. No. 5,900,342 also discloses diamond-like carbon.

[0030] U.S. Pat. No. 4,120,995 achieves a wetting angle for water of 105+/−5 degrees that is slightly better than that of Teflon™ (polytetrafluoroethylene). Other patents of interest are U.S. Pat. Nos. 5,942,317, 4,565,714, and 5,900,342. U.S. Pat. No. 5,736,249 discloses a siliconic polymer having surface energy of 18-21 dyne/cm. The following U.S. Pat. Nos. are for nozzle plates for ink-jet printing, all in a flat geometry: 5,812,158 (a low surface energy polymer coating and also a coating of tantalum instead of gold); 5,350,616 (a Kapton film); 4,643,948 (coatings for ink jet nozzles, partially fluorinated alkyl silane and a perfluorinated alkane). Other patents for coatings include U.S. Pat. Nos. 5,608,003; 5,266,222; 4,716,059; 5,942,317; and 4,565,714. Efforts have also been made to modify the surface properties of silicon for making nozzles, such as in U.S. Pat. No. 4,623,906 which discloses a wetting-resistant coating which transitions from silicon to silicon nitride to aluminum nitride, but the final surface of aluminum nitride is not adequate to resist wetting by organic solvents.

[0031] There is yet another factor which influences surface hydrohobicity, namely surface microgeometry. If a surface is made of a material that is already hydrophilic, roughness makes it more hydrophilic. Conversely, if a surface is made of a material that is already hydrophobic, roughness makes it more hydrophobic. This is described in Physical Chemistry of Surfaces by Arthur W. Adamson and Alice P. Gast (John Wiley, New York, 1997) and also in Principles of Colloid and Surface Chemistry, Third Edition, by Paul C. Heimenz and Raj Rajagopalan, (Marcel Dekker Inc., 1997). Roughness of hydrophobic surfaces is cited in U.S. Pat. No. 6,037,168, which describes rough hydrophobic surfaces for use in making inexpensive laboratory vessels.

[0032] In addition to these various geometry and surface properties, there is also yet another factor which influences swingback and may be somewhat related to the particular technique used for dispensing. It appears that the velocity or momentum of the departing liquid also has an influence on swingback. In particular, under any circumstances and for any liquid, extremely slow flow is unlikely to break away from the nozzle as a small drop but rather is likely to remain on the nozzle due to lack of momentum. If dispensing is done through a microvalve and the shutoff of flow of liquid is not abrupt but instead continues gradually after nominal shutoff, or if there is any leakage or outflow of fluid between commanded dispensings, this can aggravate or cause swingback.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0033] **FIG. 1** is an illustration of the operation of a prior art nozzle with a jewel nozzle opening and flat exit geometry.

[0034] **FIG. 2** is an illustration of the operation of a prior art nozzle with an externally tapered nozzle.

[0035] **FIG. 3** illustrates a cross section of one embodiment of a nozzle, the nozzle incorporating a pre-manufactured externally tapered end and an exterior coating in accordance with the principles of the present invention.

[0036] **FIG. 4** illustrates the surface tangent angle of the nozzle of **FIG. 3** in accordance with the principles of the present invention.

[0037] **FIG. 5** is a photograph of the dispensing end of the nozzle of **FIG. 3**.

[0038] FIGS. **6A-6C** show a sequence of operation detailing initial, steady-state, and shut-off flow of ethanol through the nozzle of **FIG. 3**.

[0039] **FIG. 7** shows the electrical waveform applied to the valves in accordance with the principals of the present invention.

[0040] **FIG. 8** illustrates a typical appearance of fluid stream with organic solvents in response to the waveforms of **FIG. 7** in accordance with the principles of the present invention.

[0041] FIGS. **9A-9C** are photographs of roughened and coated nozzles in accordance with the principles of the present invention.

[0042] **FIGS. 10A and 10B** show nozzles roughened by laser-machining circumferential grooves in accordance with the principles of the present invention.

[0043] **FIG. 11** shows a nozzle roughened by laser-machining both circumferential and slant-height grooves in accordance with the principles of the present invention.

[0044] **FIG. 12** illustrates one method of applying a coating to a nozzle in accordance with the principles of the present invention.

[0045] **FIG. 13** is a schematic view of an apparatus for applying the coating illustrated in **FIG. 12**.

[0046] FIGS. **14A-14C** illustrate cross sections of various alternate geometries of nozzles in accordance with the principles of the present invention.

[0047] FIGS. **15A-15C** illustrate a nozzle made of low-surface-energy resin as a bulk material making up the entire tip of the nozzle in accordance with the principles of the present invention.

[0048] FIGS. **16A-16C** illustrate various geometric calculations related to FIGS. **15A-15C** in accordance with principles of the present invention.

[0049] FIGS. **17A-17G** illustrate alternate manufacturing forms of FIGS. **15A-15C** in accordance with principles of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0050] A wetting-resistant nozzle, and in particular, an apparatus and corresponding method for manufacturing a wetting-resistant nozzle for use in dispensing low surface energy fluids wherein the nozzle includes an exceptionally low surface energy (hydrophobic) coating and specific nozzle geometry, is described in detail herein. In the following description, numerous specific details are provided, such as specific coatings, specific geometric nozzle configurations, dimensions, specific dispensed fluids, and the like, to provide a thorough understanding of the embodiments of the invention. One skilled in the relevant art, however, will recognize that the invention can be practiced without one or more of the specific details, or with other coatings, dispensed liquids and the like. In other instances, well-known structures or operations are not shown or not described in detail to avoid obscuring aspects of the invention.

[0051] One embodiment of the present invention includes a wetting-resistant nozzle for accurately and precisely dispensing small volumes of liquids. The nozzle comprises an internal flowpath, and an external surface that recedes from the discharge point at an angle greater than 90 degrees, and an exceptionally low surface energy for the external surface. The low surface energy material may exist as a coating on top of a shaped substrate. A flat land region may be included and may have sharp edges, one of which may define the boundary of the low surface energy region. Another embodiment includes the low surface energy material as a bulk material through which a hole is drilled. In yet another embodiment, the internal flowpath inside the nozzle may be smoothly tapered. Additional aspects such as surface roughening, surface tangent angles, coatings and geometric configurations are described herein in more detail with reference to the Figures and Examples. Nozzles in accordance with the principles of the present invention provide improved dispensing of liquids that have both low surface tension and low viscosity, such as organic solvents.

[0052] The nozzle described herein in accordance with aspects of the present invention may be axisymmetric having cylindrical symmetry around an axis. The axisymmetric external surface may be frusto-conical or it may be of other curved shape having axisymmetry. The axes of symmetry of both the internal flowpath and the external surface may be identical. The nozzle may have a surface tangent angle, as defined for particular tip geometry, which is greater than 90 degrees and perhaps substantially greater than 90 degrees.

[0053] The nozzle described herein in accordance with aspects of the present invention may be made of a bulk material which is suitable for whatever manufacturing operations may be desired to produce the desired geometry, while its surface attains the desired surface energy properties in appropriate places by means of a coating of a material having low surface energy. Alternatively, the nozzle may use a low surface energy material as a bulk material that is used to make essentially all of the nozzle tip including its surface.

[0054] Several embodiments of nozzle geometry are defined herein in according to the geometric nature of the transition between the flow passageway and the nozzle exterior. One embodiment of the nozzle includes a sharp, essentially knife-edge as the transition. Due to manufacturing limitations it should be considered that any real tip would have a transition region which is either a finite (non-zero) radius of curvature or a finite (non-zero) width of flat region, but in some circumstances the dimension of the radius of curvature or land width may be very small in comparison to the diameter of the orifice, and this can be considered a knife edge. In such a case the detailed shape of the transition region is less important to the final dispensed fluid. For example, manufacturing a knife-edge orifice would be possible if the orifice diameter were of a moderate size rather than extremely small. Appropriate regions of the nozzle would include surfaces of a low surface energy.

[0055] Alternative embodiments of nozzles have small diameter orifices such that, given the manufacturing limitations applicable to manufacturing the tip, it is not possible to attain the limiting situation of a knife-edge. In such a case, the nozzle may comprise a small land that provides minimal space for development of a persistent drop. A land is a flat region essentially perpendicular to the principal flow direction of the nozzle. A sharp edge at the outer edge of the land may help to discourage the liquid from advancing beyond that edge, as does a receding, possibly tapered (or other-shaped) exterior. Appropriate regions of the nozzles would have a low surface energy. The nozzles of the first several examples are for the case where a flat surface is deliberately manufactured at the tip.

[0056] In accordance with yet another embodiment of the present invention, there is a nozzle configuration wherein the nozzle exterior is essentially a portion of a sphere, namely, curved, having low surface energy, and then a hole is drilled through the curved material. A fairly sharp corner or edge may be assumed to exist where the hole meets the curve. Alternatively, nozzles with fillets are also possible, having low surface energy in appropriate regions.

[0057] In accordance with another aspect of the invention, another consideration that influences the wetting of a solid by a liquid is the surface energy of the nozzle surface material, or, more exactly, the comparison between the values of the surface tension of the liquid and the surface energy of the solid. Both of these properties are expressed in units of dyne/cm or equivalent units. The surface tension is a property of a liquid, which is determined largely by chemistry and can be significantly influenced by additives (e.g., surfactants). The surface energy of a solid is a material property that is determined in large part by chemistry but also is influenced to some degree by surface finish or microstructure, crystal orientation, manufacturing methods, cleanliness/contaminants, etc. If the solid surface energy is somewhat greater than the liquid surface tension, by approximately 10 dyne/cm, then wetting typically occurs. If the solid surface energy is somewhat lower than the liquid surface energy, then wetting typically does not occur. There is a range of partial wetting when the two quantities are in the same range of magnitude as each other.

[0058] In accordance with another aspect of the invention, wetting is also quantified by the contact angle. The surface contact angle is the tangent angle where the surface of a liquid drop meets the solid surface. Non-wetting is characterized by liquid droplets "beading up" when they are dispensed onto the solid surface. Contact angles approximately equal to or greater than 90 degrees are considered non-wetting or minimally wetting. Low contact angles of several tens of degrees indicate behavior that is almost wetting. At even lower contact angles or greater excess of the surface energy over the surface tension, liquids spread rapidly over the solid surface. Smaller surface energy and larger contact angle are associated with non-wetting behavior. The relation between solid surface energy, liquid surface tension and contact angle is known as Young's equation.

[0059] Under aspect of the present invention, various available formulations of low surface energy materials are discussed herein. In general, the surface could be made of any material mentioned herein or in the incorporated references which has a surface energy of 17 dyne/cm or smaller (less than that of the commonly available Teflon). A particular material which may be used here is a highly fluorinated epoxy (fluoroepoxy). A material that may be used is a material having a large fraction of terminal trifluoromethyl groups at its surface such as is available from the Cytonix Corp. Many of these are curable materials, typically heat-curable or curable by application of ultraviolet light. Another version is already polymerized and is dissolved in a fluorosolvent for purposes of application, with the fluorosolvent then disappearing by evaporation (possibly at elevated temperature).

[0060] In particular, for these materials, it is found that the surface energy is lowest on the surface that is exposed to the atmosphere while curing or drying, which is associated with the preferred orientation of the terminal trifluoromethyl group. At surfaces which are exposed after curing or drying, as a result of a machining or cutting operation, the surface energy is not so low, i.e., the material is not so hydrophobic, which is less favorable for resisting wetting. At surfaces that are cut or otherwise exposed after curing, the surface energy is approximately in the range of the surface energy of conventional Teflon. This means that design and processing techniques may be arranged so that the final surface in the desired parts of the nozzle is an as-cured surface. One way of achieving this is to apply the material as a coating on a substrate that is already in the desired final shape.

[0061] Under best conditions, the surface energy achievable with these fluoropolymers at the cured surface is 6 to 12 dyne/cm. Expressed alternatively in terms of contact angle, these substances have reached contact angles for water as high as 150 degrees. In addition, the fluoroepoxy materials are suitably hard and able to be drilled if necessary. The fluoropolymers can also be put onto a surface in a thin layer and cured to form a coating. They are also immune to organic solvents of interest including alcohols and chloroform.

[0062] Except where stated otherwise, the data presented herein is for nozzles which have been coated with a Cytonix fluoropolymer FluoroPel™ PFC1604A, involving an oligomer with a carbon chain length 5 to 18, which was applied as a liquid resin having a low viscosity similar to that of water. This substance is already polymerized and is dissolved in a fluorosolvent. In such a case heat is used to evaporate the solvent but heat is not needed for curing (i.e., polymerization). Another available formulation used for one example is designated GH000 (heat curable) with the curing causing polymerization. Ultraviolet curing formulations are also available.

[0063] In the data reported here, liquid was dispensed through miniature solenoid-operated valves. Fluid was caused to flow through the valve under action of a steadily maintained pressure from a fluid reservoir. When electric power to the valve is on, the plunger of the valve lifts up from the seat all the way or at least partway. When electrical power is off, the plunger returns and closes due to the action of a spring and also fluid pressure. Two sizes or designs of valves were used during this work. One type of microvalve had valve seats made of Viton-GF so as to be chloroform-compatible and it was used in experiments involving chloroform. The other type of valve used in the present work has the smallest seat size of any standard design currently available. In this case the seat was made of EPDM (ethylene propylene diene rubber). These latter valves were used with ethanol and ethanol-water mixtures. All data reported here were taken with the microvalve being driven by a pulse width modulated driving waveform, with a microvalve actuation frequency of 800 Hz, pulse width approximately 200 microseconds, and a voltage magnitude of pulse of 40 Volts.

[0064] The invention is further described, but is in no way limited, by the following examples.

EXAMPLE 1

Smooth, Tapered, Coated Nozzle

[0065] In one embodiment of the present invention, the nozzle design includes several features that together result in an improved wetting resistant nozzle performance. The features of the present embodiment are summarized in **FIG. 3**. The overall bulk shape or body of the nozzle is made of a material which is selected in part for its ability to be manufactured in the desired shape. The desired surface properties may be obtained by applying a coating to selected places on the nozzle.

[0066] **FIG. 3** illustrates one nozzle configuration in accordance with the principles of the present invention. The nozzle **300** has an external surface **310**, an internal passageway or flowpath **320**, an inlet **305** and an outlet **315**. The internal flowpath **320** in the present embodiment is smoothly contoured and tapered to allow laminar flow of fluid. The external surface **310** includes a sharply angled exterior surface **330**, a coating **340** applied to the external surface **310** between the angled exterior surface **330** and the outlet **315**, and a land region **350** at the outlet **315**. The exterior surface **330** may optionally be surface roughened before applying the coating **340**. The external surface **310** may be axisymmetric. The axisymmetric external surface **310** may be frusto-conical as shown in the present embodiment.

[**0067**] In this example, the transition region between the internal passageway **320** and an external axisymmetric surface **310** is a small flat region that is essentially perpendicular to the axis of the internal flowpath **320**. This flat region may be referred to as the land **350**. This geometry is easier to manufacture than a knife-edge or even a rounded knife-edge, partly because it provides a chance for dimensional errors to be absorbed simply as irregularity of the dimension of the land. For example, if the external surface is highly tapered, minor dimensional errors in the coaxiality of alignment of the internal passageway with the external surface would cause a knife-edge to wander seriously out of plane or circularity, whereas with the use of a flat land such errors would merely cause the annular land to have a minor amount of eccentricity while the land would remain in a well defined plane. Keeping the exit plane perpendicular to the flow direction has more impact on flow than keeping the interior edge and the exterior edge of the annulus perfectly concentric with each other. Eccentricity of the land has a much less serious impact on dispensing geometry than would be the impact of a knife-edge wandering out of plane.

[**0068**] A flat land is defined by where it meets or adjoins two other surfaces: the internal passageway **320** and the external axisymmetric surface **310**. The angle at which it intersects either of those other two surfaces is defined as being 90 degrees at the interior, and at the exterior it is less than 90 degrees but can be close to 90 degrees. It is known that sharp corners or edges, such as where the land meets the exterior, can arrest the spread of a liquid on a surface. Because of the use of a design with a flat land, the edges where the land adjoins those other two features may each be designed to be substantially sharp. The term sharp is used with the realization that, at some size scale, any real edge has some detail that may approximate a rounded edge having an edge radius. For the present embodiment, a substantially sharp edge means that the edge radius may be small compared to the lateral dimension (outer radius minus inner radius) of the land, such as edge radius being less than one-fifth of the lateral dimension of the land.

[**0069**] The land **350** is made as small as possible compared to the diameter of the orifice or outlet **315** in order to minimize space available for a puddle to form. The land is typically a result of a particular manufacturing process and cannot realistically be of zero width, but for purposes of the present embodiment, is minimized. Therefore, for some sets of nozzle dimensions, the land dimension may be determined by being the smallest dimension that is practical for manufacturing. An approximate manufacturing limit is believed to be the outside diameter minus the inside diameter being no smaller than approximately 0.001 inch. The nozzles for which experimental results are reported in this example include a small flat land.

[**0070**] **FIG. 3** further illustrates an interior flowpath of the nozzle **300** wherein the flowpath includes an angle **380** and a taper **385**. The taper **385** transitions the internal flowpath from an inlet diameter ID down to the outlet diameter D of the nozzle at the outlet **315** for dispensing. A gradually tapering internal flowpath **320** helps to achieve a good quality dispensed flow because it minimizes flow disturbances that might be created in the flow just before it exits from the orifice. Nozzles have been tested which had a more abrupt entrance to the final narrow hole, and these other nozzles had a greater tendency to exhibit split-streaming. With the nozzles as shown here, the internal flowpath **320** is tapered at an angle typically less than or approximately equal to 10 degrees total included angle. The internal flowpath **320** may have a constant-diameter flowpath for a small distance immediately back from the nozzle exit, such as several diameters of the exit hole, and, preceding that, a gradual taper of the described angle.

[**0071**] In yet another embodiment of the present invention, the surface of the internal flowpath or passageway **320** has a relatively large surface energy, namely, a wettable or hydrophilic surface. The hydrophilic surface encourages the liquid to occupy an acceptable place in the nozzle, in contrast to the unacceptable presence of liquid on the external surface of the nozzle.

[**0072**] **FIG. 4** illustrates surface tangent angle SA for a nozzle **400**. In specifying a nozzle design, one geometric specification is the surface tangent angle SA. One ray of this angle is the flow vector that is typically the direction of discharge of flow along the axis of symmetry **405** of the flow passageway **410** in the nozzle **400**. The other ray is a ray, coplanar with the first ray, which goes through the corner where the land **415** meets the nozzle external surface **425**, and is tangent to the nozzle external surface **425** at that point. This surface tangent angle SA is greater than 90 degrees, and may be substantially greater than 90 degrees. For example, the surface tangent angle SA may be as large as 165 degrees or even 170 degrees. In the nozzle **400** shown in **FIG. 4**, the conical exterior has a total included angle **420** of 30 degrees (half-angle **430** being 15 degrees), which means that the external surface angle **410** with respect to the flow direction is 165 degrees.

[**0073**] There is a certain distance back from the tip of the nozzle at which the features of the present invention, such as surface tangent angle and surface energy, have an effect. Beyond that distance it is no longer important to maintain those features of the present invention and it is possible to depart from those features with no adverse impact. For example, beyond such distance it is possible to depart from the frusto-conical shape, and it would also be possible to change to a surface composition or other surface property so as to be not as hydrophobic as in the region near the tip. For example, such a distance would be related to the largest distance that liquid is capable of swinging back, or the largest drop that forms if swingback does occur. Such a distance away from the exit may be estimated as 0.5 inch for typical dimensions of small nozzles for 3DP printing applications.

[**0074**] In the nozzles of the present embodiment, a sharp corner is where the surface properties change from the moderately-wetting or highly-wetting surface energy of the land to the lower surface energy of the hydrophobic external surface. This abrupt physical edge and materials change provides two disincentives to the further spread of fluid, namely, the sharp change of angle and the change to a much more hydrophobic surface.

[**0075**] Therefore, the coating procedure is conducted so as to attempt to cause the resin to stop specifically at the sharp comer or edge where the conical exterior meets the land, but not to coat the land. If the land is small, it is acceptable for the land to be of a relatively high surface energy. In fact, as described, the presence of a small land of relatively high surface energy may even be helpful in controlling swing-back of drops. The land may provide a place for excess fluid to collect that might otherwise swing back onto the exterior cone. The use of a sharp edge where the land meets the external surface may serve the purpose of arresting the spread of fluid on a solid; namely, to discourage liquid on the land from spreading onto the conical exterior.

[**0076**] The coating material applied to the nozzles of this example was Cytonix FluoroPel PFC 1604A, which is a relatively low viscosity formulation, with heating in accordance with the manufacturer's instructions

[**0077**] The overall bulk shape or body of the nozzle may be made of a material that is selected in part for its ability to be manufactured in the desired shape. Examples of suitable bulk materials include tungsten carbide and also other ceramics, metals, silicon and polymers. Manufacturing processes appropriate to various of these materials for purposes of making the desired nozzle shape include machining, drilling, various forms of EDM, etching, molding/casting, etc. The desired surface properties may be obtained by applying a coating to selected places on the nozzle.

[**0078**] The nozzles of this embodiment were made of tungsten carbide. Tungsten carbide can be manufactured into varied and complex geometries by sintering powder together. Tungsten carbide can be ground to provide finer resolution and is electrically conductive. The electric conductivity means the tungsten carbide can be cut by Electrical Discharge Machining so as to make cuts that are accurately dimensioned, sharp-edged and burr-free. Tungsten carbide has a relatively large surface energy, which is not a useful property for the vast majority of the external surface when fluid is being dispensed. Therefore, the nozzles of the present embodiment were coated, such as with the Cytonix material, to provide low surface energy on appropriate surfaces. Having the uncoated regions such as the small exposed land and the interior of the flow passageway be of relatively large surface energy (hydrophilic or wetting) may be of some use in encouraging the last segment of liquid to remain in those places rather than swinging up onto the exterior cone surface. For example, this surface may have a surface energy of 50 dyne/cm or greater.

[**0079**] **FIG. 5** illustrates a nozzle outlet in accordance with the above-described embodiment. The nozzle is made out of tungsten carbide, and had a coating of fluoropolymer resin applied to its external conical surface. The nozzle has a land outside diameter OD of 0.012 inch (305 microns), an outlet hole inside diameter ID of 0.0107 inch (272 microns), exterior coated with fluoroepoxy. Alternative dimensions include, for example, combinations of orifice diameter and land outside diameter, respectfully, of: 0.004 inch, 0.005 inch; 0.003 inch, 0.0045 inch; 0.002 inch, 0.003 inch; and 0.001 inch, 0.002 inch.

[**0080**] FIGS. **6A-6C** are frames of videos of various flow regimes through the nozzle of **FIG. 5**. The photos in FIGS. **6A-6C** are a sequence of successive frames from a video, taken at around the time of shutoff of the programmed sequence of valve pulses. **FIG. 6A** is a photo of a nozzle dispensing a fully-established non-wetting flow of pure ethanol through the nozzle. **FIGS. 6B and 6C** are successive frames of video at a speed of 30 frames per second depicting the shutoff sequence of the nozzle dispensing the pure ethanol stream. In **FIG. 6**A, flow is still fully established. In **FIG. 6B, a** wisp of fluid appears some distance downstream of the nozzle, but there is no fluid immediately at the nozzle. In **FIG. 6**C, fluid has stopped flowing out of the nozzle, and whatever fluid already left the nozzle has fully detached from the nozzle and has left no swingback or drop on the nozzle.

[**0081**] Videos of flow through the nozzle show that there is a very small probability of swingback happening at the time of turning on a stream, and that the most likely time for a drop to swing up and attach to the exterior cone is at the time of shutoff. The present embodiment described herein uses microvalves pulsed at 800 Hz. Programmed operation of the microvalve is intermittent, with approximately 50 consecutive valve actuations at intervals of 1/800 sec., followed by a somewhat longer quiet period.

[**0082**] **FIG. 7** illustrates a graph of a typical electrical waveform applied to a microvalve shown as a Pulse as a function of Time. In the current embodiment, a pulse **710** is sent for a time T_1 to open the valve and begin flow. A period of no pulse or voltage **720** for a period of time T_2 follows in which the valve is off.

[**0083**] **FIG. 8** illustrates flow from a nozzle pulsed by the waveform of **FIG. 7**. During the time that a pulse was being dispensed, the stream appeared to issue from the nozzle **800** as a connected string of bulges **810**, even though the microvalve was being discretely pulsed, namely, turning on and off repeatedly, being on for a time T_1 of typically 200 microseconds followed by off for a time T_2 of typically 1050 microseconds. Such discharge is characteristic of fluids of certain combinations of properties as defined by the Ohnesorge number.

[**0084**] Experiments in accordance with the present embodiment produced good coherence of streams issuing from the nozzle. Usually the stream not only was coherent when it issued from the nozzle but also remained essentially just as coherent one inch or even several inches below the nozzle. This was due in part to the smooth and very gradually tapering internal flowpath inside the nozzle.

EXAMPLE 2

Roughness Made by EDM Roughening or Other Random-Roughness Methods

[**0085**] Yet another embodiment of the present invention continues to use the overall geometric features and the hydrophobic materials of the nozzle design of the previous embodiment, while incorporating surface roughness, described earlier in very general and brief terms. In general, this alternative embodiment and those described in this application are substantially similar to previously described embodiments, and the same reference numbers identifies common elements and steps. Only significant differences in construction or operation are described in detail.

[0086] The nozzle of the present embodiment takes advantage of the theoretically predicted increase in apparent hydrophobicity due to surface roughness by making a surface that is both rough and of low surface energy. In the present embodiment, roughening a bulk piece of hydrophobic material has not done, although it could be done for applications dispensing relatively easy fluids not requiring the extreme lowest surface energies. The reason the bulk piece is not roughened is because the leading candidate resins are not as hydrophobic as would be desired when below-surface material is exposed. Therefore, the nozzles of this embodiment were produced by making a nozzle body or substrate which is rough in desired places, and then coating those places with the hydrophobic material of interest in such a way that the final surface of the coating also had at least some of the surface roughness features of the substrate. In this way the final rough surface was an as-cured surface having the preferred orientation of molecules at the surface. In this example the coating material was the fluoropolymer but it could also be any of the other related substances that are discussed herein.

[0087] This nozzle of this embodiment was manufactured by manufacturing the nozzle with a smooth surface and then roughening the surface in a random pattern. This example used a form of EDM or spark erosion to roughen the surface of the nozzle. This is possible because the tungsten carbide, of which the nozzle was made, was electrically conductive. In it, the electrode was a closely fitting mating shape which was rotated with respect to the nozzle, and as current flowed, sparks at the interface between the electrode and the nozzle caused erosion of the nozzle. The dimensions of the surface roughness or texture produced by this process appear to be on the order of single digits of microns.

[0088] After such a rough substrate has been created, the surface coating for this embodiment should be such that at least some of the substrate roughness is apparent on the coating surface. For example, the coating thickness dimension must be small enough so as not to fill up or smooth out the depressions in the patterned or roughened surface. Accordingly, a resin of relatively low viscosity is used. The resin used was FluoroPel(™) PFC 1604A from Cytonix Corp. After a coating of this liquid resin was applied, a jet of compressed gas was directed against the coating in a direction away from the tip of the nozzle so as to thin out the coating layer while it is still liquid by pushing some of the liquid to a place where the coating thickness is not important or excess liquid can be removed. After this was done, heating to 60-80 C. was performed according to the manufacturer's instructions to evaporate the solvent or cure the resin.

[0089] **FIG. 9A** shows a nozzle **900** of the present embodiment as originally manufactured with a smooth exterior surface **910**. In this photograph, the diameter D of the orifice is 0.005 inch (127 microns). **FIG. 9B** shows the nozzle with a roughened exterior conical surface **920**. The roughening is accomplished by electrical discharge from a rotating closely fitting mating surface (electrode) EDM. The estimated characteristic dimension of this roughness, average feature-to feature distance, or average depth of roughness, is in the single digit microns. **FIG. 9C** shows the nozzle of **FIG. 9B** coated with the described hydrophobic coating **930**. As illustrated, the coating has a sufficiently low viscosity such that the resin does not completely fill up or smooth over the roughness.

[0090] Alternatively, a similar random roughness on the surface by abrasive mechanical means could be created by sandblasting, abrasive water jet, rubbing with sandpaper or abrasive (which may be selected so as to be harder than the material of the nozzle), and the like. It would also be possible to prepare a rough surface by adding material onto an originally manufactured smooth surface, such as by adhering grains of particulate matter of a suitable size using a suitable adhesive. In any of these cases, the coating would then be applied as previously described.

[0091] Additionally, instead of forming a coating by application of liquid, it would be possible to use any of the coatings which are known as being formed by a process amenable to gaseous deposition, such as formation of diamond-like carbon followed by fluorinating by reaction with a fluorine-containing gas, or the formation of the poly-p-xylylene coating known as Parylene. Such processes, involving only gaseous substances, are adapted to coating minute surface features and very closely following the shape of the surface features. These coating options apply as well to the laser-machined examples that follow and in general to any nozzles of the present invention.

EXAMPLE 3

Roughness Made by Laser-Machining, Having Predetermined Geometry, Circumferential Grooves

[0092] Yet another embodiment of the present invention creates surface roughness, in specific predetermined geometries. Removing portions of the tungsten carbide material, making grooves or similar relieved features by laser machining, provide the roughening in this embodiment. The method of laser machining used is photoablation/decomposition, which is said to be superior to melting/evaporation in terms of cutting quality.

[0093] In accordance with aspects of this embodiment, the positions and dimensions of material that is either removed or left undisturbed can be predetermined and controlled quite accurately by the programmed position of the laser beam during the laser machining process. Feature sizes such as 0.001 inch are possible. It is believed that for structural integrity an appropriate value of the groove-to-groove thickness of remaining material (i.e., distance from the interior machined wall surface of one groove to the corresponding surface of the adjacent groove) is at least approximately 0.0005 inch, for structures manufactured by this method. An appropriate depth of groove is 0.001 inch (25 microns).

[0094] A laser-machined roughness pattern which has been found to work reasonably well for purposes of enhancing wetting resistance is a depth of groove of 0.001 inch (25 microns), a width of groove of 0.001 inch (25 microns), and a remaining wall thickness between grooves of 0.0005 inch (13 microns). This results in a situation where only a relatively small fraction of the original surface (such as one-third) survives undisturbed to form high spots, while the rest of the original surface is recessed, which is believed to be helpful, Dimensions such as these have been used with good results.

[0095] It can be appreciated that if a roughness pattern is going to be machined into the conical surface by removing material from that surface, it is necessary to start with a greater thickness of the land and the nozzle wall than would be used in the non-rough strategy. Sufficient land and wall thickness must be provided to avoid having the laser-machined grooves puncture into the internal flow passageway thereby creating leaks. For a groove whose depth is nominally 0.001 inch, the bare minimum requirement is that the land outside diameter be greater than the orifice diameter by 0.002 inch (51 microns), in which case the bottom of the laser-machined groove would just start to break through into the interior passageway, assuming there were no dimensional inaccuracy in the groove depth and no eccentricity of the internal flowpath with respect to the nozzle external surface. Practically speaking, some additional amount of material remaining between the bottom of the laser-machined groove and the internal flow passageway will remain. Additionally, this material allows for possible dimensional inaccuracy and eccentricity, in order to avoid puncturing into the internal flowpath.

[0096] When a groove is laser-machined to a nominal depth of 0.001 inch (25 microns), it is satisfactory to start with a land outside diameter which is 0.005 inch greater than orifice inside diameter, leaving a nominal wall thickness of 0.0015 inch between the base of the groove and the internal passageway. This leaves enough of a margin against cutting too deep and puncturing. Slightly smaller margins might also be satisfactory. Of course, for typical nozzle designs, as one goes farther away from the tip, the internal flowpath widens less steeply than the exterior of the cone, and so the wall thickness improves as one goes further away from the tip.

[0097] After the laser-machining operation, the nozzles may be coated with Cytonix PFC 1604A, which is a low viscosity formulation. In order to thin out the deposited resin and retain as much as possible of the initially rough topography when the coating process is completed, a jet of clean dusting gas is directed at nozzles just after they are coated with liquid resin, in a direction away from the tip. Curing of the resin is then performed according to the manufacturer's instructions.

[0098] **FIGS. 10A and 10B** illustrate laser machined nozzles. **FIG. 10A** is a photograph of a nozzle that has been laser machined in accordance with the above description. **FIG. 10B** illustrates the same laser machined nozzle coated with a low viscosity coating.

[0099] In the present embodiment, laser machining has been used here to remove material in predetermined patterns having small feature dimension. However, alternate methods of achieving the same structure including photolithography and similar techniques known from the microelectronics fabrication industry, or even by programmed wire EDM machining using fine wire. The method of material removal may be somewhat dependent on the selection of the material into which grooves or roughness are being cut. It would also be possible to create surface roughness of predetermined geometry by addition of material (such as by adhesion of particles or by vapor deposition or plating) onto an initially smooth surface rather than by removal of material.

[0100] One parameter for roughness-enhanced hydrophobicity is the ratio of the actual final surface area including all the recesses and protrusions, compared to the original or projected or flat surface area. The projected surface area is the area that exists, without the surface irregularities, when viewed looking normal to the overall surface. The larger the ratio of actual surface area to projected surface area, the greater the improvement in hydrophobicity compared to a flat unmodified surface. There are formulas in the literature of surface science where this ratio appears as a parameter. Another way of describing the same phenomena is to imagine that perhaps droplets rest only on peaks, and if the area of peaks is small compared to the area of the unmodified surface, then the improvement is substantial. Either way of looking at the phenomenon provides the same insight as to how to maximize its effect, namely by making the surface geometry more extreme and irregular.

EXAMPLE 4

Crossed Laser-Machined Grooves

[0101] The preceding example suggested that roughness-enhanced hydrophobicity benefits from a more extreme, irregular surface such as by having only a relatively small fraction of the original surface survive. The previous example accomplished this in a one-dimensional sense with parallel grooves being created in only one direction, namely, circumferential. There is probably some limitation as to how far this trend can be carried in a one-dimensional sense, because at some point the actual width of the groove might have to become impractically large, such as comparable to the natural dimension of a drop of dispensed liquid.

[0102] Accordingly, yet another embodiment of the present invention is to make this groove effect more pronounced by making intersecting cuts in two approximately orthogonal directions, so that the ridges of the preceding example become essentially interrupted ridges or, as a limiting case, spikes or bristles.

[0103] Accordingly, nozzles were made with a crossed pattern of laser-machined grooves machined in two mutually orthogonal directions rather than just circumferential grooves. The circumferential grooves were as described in the preceding example, with a groove depth of 0.001 inch and a groove width of 0.001 inch and a groove-to-groove spacing or remaining wall thickness of 0.0005 inch. The second group of grooves may be termed slant-height grooves because they exist on the slant height of the cone. They were also 0.001 inch deep and 0.001 inch wide. This resulted in a pattern in which the most-elevated remaining features of the original conical external surface were islands or interrupted ridges rather than continuous ridges. The crossed grooves removed a greater fraction of the original surface by removing material from two directions instead of just one direction.

[0104] It can be appreciated that if a certain number of slant-height grooves, having constant groove width, are designed so as to remove a certain fraction of the circumference of a ridge at the tip of the nozzle, then as the cone becomes wider further from the tip, the fraction of the ridge which is removed will not be as large and the circumferential dimension of those remaining ridge segments will increase. Eventually the length of ridge segments will increase to the extent that the fraction of a circumference removed by the slant-height grooves may no longer be significant. At this point it may be worthwhile to introduce an additional set of slant-height grooves (such as one groove between each of the already-described slant-height grooves), that start some distance away from the tip of the nozzle where there is sufficient room. If necessary, as one goes even further from the tip, yet another set of slant-height grooves can be introduced, and so on.

[0105] **FIG. 11** is a photograph of a nozzle having laser-machined grooves in both directions. One set of slant-height grooves begins immediately at the tip of the nozzle, and a second set of slant-height grooves begins some distance away from the nozzle tip where there is sufficient room for an additional groove. This nozzle in **FIG. 11** is not yet coated. The nozzles were then coated with Cytonix resin as described in preceding examples. The slant-height grooves are shown as being straight lines but could also be curved lines if desired.

EXAMPLE 5

Experimental Results Concerning Swingback

[0106] In accordance with yet another embodiment of the present invention, swingback of the nozzle is minimized or eliminated. One way of comparing the performance of various different nozzles is to list conditions for which each type of nozzle does or does not experience swingback. As already described, swingback is deposition of some liquid on the tapered exterior surface of a nozzle. Although swingback has occasionally been observed to a very minor extent at startup of flow, it is primarily a phenomenon associated with the shutoff of flow.

[0107] Instead of all the dispensed liquid continuing to proceed from the nozzle toward the target at the time of shutoff, sometimes the last little bit of liquid to pass through the nozzle does not detach from the nozzle, and does not travel toward the target, and instead ends up on the outside of the nozzle as a result of a rather large change in the direction of its motion. This is undesirable because it results in a sustained drop on a surface of the nozzle (such as the conical exterior) that is usually asymmetrical and is near enough to the intended exit path of liquid that it can interact with subsequent dispensed liquid. A sustained drop in that location can pull later exiting liquid away from its intended path, making for inaccurate direction of travel of liquid and hence inaccurate position of printing. Also a large swung-back drop can itself detach from the nozzle occasionally at unpredictable times and fall onto the surface being printed, which might ruin a printed part.

[0108] Sometimes one shutoff event is enough to produce a large sustained drop on an initially dry nozzle exterior. In other circumstances, sometimes a sustained drop grows very slowly with each shutoff event and only becomes a problem after many shutoffs. Unless otherwise noted in the table, a notation of swingback in this example indicates that one shutoff event is sufficient to produce a swingback of a significant size.

[0109] In Table 1, the vertical axis represents (from top to bottom) a sequence of increasing degree of difficulty for liquid to dispense and break off cleanly at the end of a commanded flow or series of drops. The ordering of degree of difficulty can perhaps be best understood by thinking in terms of how much momentum the last piece of liquid has coming out of the nozzle at the time of shutoff, on the thought that such momentum helps to pull or carry the liquid away from the nozzle in opposition to surface tension forces which tend to make it swing up and back. The first case in this axis of the table, which is easiest case for avoiding swingback, is the case of continuous flow dispensing, also known as line-segment printing. In this case the valve remains open continuously for a substantial length of time and so steady-state continuous pressure-driven flow exists. In line-segment printing the flowrate and consequently the liquid average velocity is as large as it can possibly be under given fluid reservoir conditions.

[0110] The next, slightly more difficult case is a pulse train whose length is a very large number of pulses. In this mode of operation the microvalve is energized by an electrical waveform having a pulse width that is about 20% of the duration of one cycle, and then for the remainder of the cycle it is not energized, and this pattern is repeated for many consecutive pulses. This is an attempt to produce a fluid stream that is a succession of discrete drops. However, for the organic solvent liquids used here, the appearance of the dispensed fluid stream, at any distance from the nozzle short enough to be useful in three dimensional printing, is believed to be connected bulges rather than discrete individual drops as already described in **FIG. 8**.

[0111] When the pulse train contains a very large number of consecutive pulses, this means that the situation regarding flow and form of fluid structures has reached quasi-steady-state and there is no influence of any possible startup transient which might last for some number of cycles or pulses. The fluid stream contains an average fluid exit velocity that is some fraction of what it was in the case of line-segment printing, somewhat reflecting the fact that the valve is open for only a fraction of the overall time. In the situation that exists after a substantial number of consecutive actuations, this (average) exiting velocity is as large as it can possibly be for pulsed operation.

[0112] Cases of further increasing difficulty are when the number of pulses in each pulse train is finite and becomes smaller and smaller. In between the described pulse trains are time intervals of sufficient length that there is no carry-over effect from one pulse train to another. It has been observed in calibrations of flowrate for pulsed operation of microvalves that there is a correction factor describing the fact that the flowrate (during the time that flow is on), or volume per drop, becomes smaller as the pulse train becomes shorter and shorter. The correction is in the range of 10% to 15% for the shortest pulse trains compared to very long pulse trains. It is believed that this correction illustrates the existence of a startup transient at the beginning of a pulse train, implying that there is less momentum contained in a short pulse train than in a pulse train that is long enough to have reached quasi-steady-state. This decreased momentum for shorter pulse trains probably also makes for more difficulty as far as clean breakoff of fluid from the nozzle. Of course, for a nozzle to be able to print finely detailed features such as in 3DP, it is desired that flow be able to shut off cleanly without swingback even for rather short numbers of pulses in a pulse train.

[0113] The other axis of the table is a progression of degree of roughness of the external conical surface of the nozzle, which is further elaborated by listing results for two different fluids to also illustrate a sort of progression in terms of difficulty of the fluid for non-wetting purposes. The progression in this axis of the table is based on the belief that rougher is better, at least for dispensing pure solvents. The first three columns in the table form a progression from smooth to slightly rough to rougher. The progression of roughness is from a smooth surface to an EDM roughened surface to a surface with laser-machined grooves in only the circumferential direction. In the last column of the table, the progression further advances to a surface with laser-machined grooves in two mutually orthogonal directions. All of the surfaces are coated with a low surface energy coating.

[0114] In this table, the first column is for a nozzle whose exterior was smooth as purchased, and was coated with Cytonix. The slightly rougher situation for a nozzle that was EDM-roughened and then coated with Cytonix. This surface was somewhat rougher but was not an extreme amount of roughening. The next column was for a still rougher nozzle that was laser-machined with circumferential grooves and was then coated with Cytonix. It was a nozzle of 0.003-inch inside diameter, 0.011-inch land outside diameter, laser-roughened with groove width and ridge width around 0.001 inch depth of groove half to 1 thousandth of an inch, coated with Cytonix PFC 1604A (low-viscosity). The crossed groove case in a later column had similar size grooves in the other direction as well. The crossed-groove design had circumferential grooves dimensioned as 0.001-inch deep and 0.001-inch wide with 0.0005-inch thickness of wall or remaining material between grooves. The slant-height grooves were similar with a spacing which permitted the ridge segments to be slightly longer than wide, near the tip of the nozzle, with further increases in segment length further away from the tip. All laser-machined nozzles had orifice diameter 0.003-inch (76 microns). For data in this table, all nozzles had a total included angle of 30 degrees.

[0115] The generally observed ranking of the fluids is that ethanol is an easier fluid and chloroform is a more difficult fluid as far as avoiding wetting. Because of this pattern, one of the better nozzles for ethanol is repeated for the more difficult chloroform, and after that is included the still rougher design of nozzle having crossed laser-machined grooves.

[0116] The following table contains the experimental observations concerning swingback, reported as observations of conditions that do or do not result in swingback after repeated shutoff of pulse trains. This observation is of usage which is very closely related to the intended use of the nozzles, which is for 3D printing articles such as dosage forms which often include fine printed features having a dimension which is thin along the fast axis of motion. The table shows how short a pulse train can be delivered while remaining free of swingback, which implies how thin a 3D printed wall or feature would be practical by printing with such a nozzle.

[0117] The first column or nozzle design (smooth +coated, with ethanol) provided swingback-free shutoff only for line-segment and continuously pulsed operation. The second column (EDM-roughened +coated, with ethanol) provided swingback-free shutoff for line-segment, for continuously pulsed and for pulse trains as short as approximately 24 consecutive pulses. The third column (laser-machined with circumferential grooves +coated, with ethanol) provided swingback-free shutoff for line-segment, for continuously pulsed, and for pulse trains as short as approximately 4 consecutive pulses, which is just about short enough to be useful for building walls of oral dosage forms. Thus, for these three ethanol cases, the rougher the surface the better is the performance in resisting swingback.

[0118] The fourth column shows the same nozzle as column 3 but used with chloroform. Compared to column 3, there was degradation of performance, in that swingback-free shutoff with chloroform could only be achieved for line segment, for continuously pulsed and for pulse trains longer than approximately 300 consecutive pulses. This is worse than the ethanol results, in which swingback-free operation was achieved for pulse trains as short as 4 pulses. With chloroform and these nozzles, pulse trains shorter than 300 pulses resulted in formation of a drop on the outside of the nozzle. Thus, the further roughening feature of crossed grooves was tested with chloroform, and performance improved to being able to shut off chloroform swingback-free at a pulse train as short as 50 pulses. Operation of these nozzles with chloroform at somewhat less than 50 consecutive pulses did not result in immediate swingback, but after many shutoffs a swung-back drop did develop on the conical surface. In this table, the notation clean means clean breakoff of drops upon shutoff with no swingback, and is the desired state.

TABLE 1

Performance of nozzles with pure ethanol and pure chloroform

Short description of surface	Smooth	Slightly rough	Moderately rough	Moderately rough	Greatest roughness
Liquid	Ethanol Smooth + Cytonix	Ethanol EDM rough + Cytonix	Ethanol Laser rough Circumferential + Cytonix	Chloroform Laser rough Circumferential + Cytonix	Chloroform Laser rough Crossed grooves + Cytonix
Line segment	clean	clean	clean	clean	clean
Continuously pulsed	clean	clean	clean	clean	clean
Pulse train 300 pulses	forms drop	clean	clean	clean	clean
Pulse train 200 pulses	forms drop	clean	clean	swings back	clean

TABLE 1-continued

Performance of nozzles with pure ethanol and pure chloroform

Short description of surface	Smooth	Slightly rough	Moderately rough	Moderately rough	Greatest roughness
Pulse train 50 pulses	forms drop	clean	clean	swings back	clean
Pulse train 24 pulses	forms drop	clean	clean	swings back	swings back
Pulse train 6 pulses	forms drop	slow drop	clean	swings back	swings back
Pulse train 4 pulses	forms drop	slow drop	clean	swings back	swings back
Pulse train 2 pulses	forms drop	forms drop	swings back	swings back	swings back

[0119] When all of the entries in this table are taken together, they define regions of parameter space in which wetting-free operation can be expected or should not be expected.

EXAMPLE 6:

Nozzle With Complicated Fluid Containing Solute (Smooth, Sharply-Angled Nozzle)

[0120] In accordance with yet another embodiment of the present invention, a nozzle for dispensing complicated a fluid-containing solute is described. The binder liquids that were used in the preceding examples (ethanol and chloroform) were simple pure solvents that might be called prototypical of binder liquids that would be dispensed for purposes such as manufacturing medical articles. The fact that they are pure solvents means that if any drops or splashes occur and the solvent evaporates, nothing is left behind on the surfaces that received the drops or splashes.

[0121] Binder liquids actually dispensed in the fabrication of medical products by 3DP are likely to have additives dissolved in them that result in somewhat different fluid properties. Such binder liquids are likely to require some amount of additional characterization work. One example of a more complicated binder liquid that has been tried is a solution containing 64% ethanol, 21% water, and 15% triethyl citrate (a plasticizer), having a surface tension of 26 dyne/cm and a viscosity of 1 to 2 centiPoise.

[0122] It has been found that for this liquid, roughness of the coated exterior of the nozzle did not enhance hydrophobicity as it did for pure solvents. For this particular fluid, it has been found that the fluid wet the roughened coated surfaces rather easily, which is a contrast to the results for pure solvents. For this particular fluid it was found to be preferable to use a smooth-surfaced, coated nozzle such as was described in Example 1. In particular, it was found that under those circumstances a taper of 20 degrees total included angle for the conical external surface worked better than a taper of 30 degrees. It is believed that even smaller total included angles may be even better. It is also believed that, at least for this family of substances, more dilute solutions are easier than more concentrated solutions as far as dispensing without wetting or swingback. For complicated fluids such as these, optimum wetting-resistant nozzle design may depend on the constituents of the fluid and their concentration.

EXAMPLE 7

Nozzle Coating Apparatus

[0123] In accordance with yet another embodiment of the present invention, a method and apparatus for coating the nozzles previously describe herein is shown and described. For certain sizes of nozzles, it is possible to apply the coating to the nozzle external surface using an applicator by hand, possibly while working under magnification. However, improved control of coating placement can be achieved if some sort of positioning apparatus is used. Such apparatus may be constructed of commercially available optical breadboarding and positioning apparatus. It may include a rotary table for mounting and rotating the nozzle, since the nozzle is axisymmetric, and apparatus such as a multidimensional precision motion stage for positioning an applicator, and may further include a magnifying visual system.

[0124] In applying liquid coatings at dimensions as small as those of interest here, an important influence is the behavior of the surface of a drop of coating resin or liquid in contact with a solid, with the shape and position and motion of the liquid drop showing the influence of the surface tension of the liquid. The nozzle coating apparatus and technique take advantage of the surface-tension-dominated behavior of liquids involving the advance and recession of small drops on solid surfaces.

[0125] When a liquid such as a drop contacts a solid surface, there is a contact angle that is determined principally by the relative values of the liquid surface tension and the solid surface energy and is described by Young's Equation. This behavior includes the existence of an advancing contact angle, for which a drop is on the verge of advancing, and a receding contact angle, for which a drop is on the verge of receding. Between these two limiting angles is a range of angles such that the contact angle of the liquid on the solid can have any value between these two limiting angles without the position of the liquid edge advancing or receding or changing its position at all.

[0126] This description so far describes the behavior of a drop of liquid on a flat smooth solid surface. For a geometry which includes a sharp convex edge, when a liquid drop reaches the sharp convex comer or edge, it hesitates at the sharp convex corner or edge and the position of its edge or the extent of its advance is defined by the sharp convex comer or edge. This behavior has already been described in regard to control of wetting at the nozzle tip, but it is also relevant and useful for the positioning of the edge of resin as part of the nozzle coating process. When the edge of a liquid puddle or drop, in this case made of resin, is at a sharp convex comer or edge, the difference between contact angle for advancing past the comer or edge and the contact angle for receding from the comer or edge can be substantially larger than simply the difference between the advancing and receding contact angles on a flat surface. This makes it easy to define the edge of an applied liquid coating by a sharp convex edge. Such hesitation behavior would not be apparent, or would be much less apparent, if an edge were a gently curved surface, as opposed to sharply cornered.

[0127] Thus, the geometry of the nozzle itself can be used in defining the edge of the region upon which the coating is applied, just as the sharpness of the edge together with the change of surface energy (created by the present method) later helps to define the edge of the possible puddle during dispensing. If the desired position of the edge of the coating coincides with a sharp edge, then the position of the coating edge can be largely defined by the as-manufactured sharp edge, with the result that the position of the coating edge becomes far less dependent on positional accuracy of the applicator, or even the skill of the operator, than would be the case if the desired coating edge were at a more ordinary place. This fact allows precision in coating placement and achievement of the desired design of spatial pattern of surface energy, which can help to direct dispensed liquid to remain in certain regions and avoid other regions.

[0128] **FIG. 12** illustrates one embodiment of a technique suitable for applying the low-surface-energy resin to the exterior conical surface of a nozzle. Steps **1-6** of **FIG. 12** can be viewed as steps that are performed at one angular location at a time, or they can be viewed as steps that are performed as the nozzle surface undergoes rotation around its axis of symmetry.

[0129] Step **1** shows, in cross-section, a bare nozzle **1200** before any coating is applied. The conical nozzle is shown pointing vertically upward so that gravity will pull the resin away from the tip.

[0130] Step **2** shows a drop of resin **1210** as it is brought into contact with the external conical surface **1220** using a small sharp applicator **1230** such as a pin. The resin **1210** is brought into contact with the external conical surface **1220** a slight distance below the nozzle tip **1240**.

[0131] Step **3** continues after step **2** and shows that the drop of resin **1210** may then be nudged upward by the upward motion of the applicator **1230** in a controlled manner. When the drop of resin **1210** reaches the sharp external edge **1240**, which is the meeting place of the land **1250** and the external surface **1220**, it hesitates and forms a slight bulge, as typically occurs due to surface tension when any liquid meets a sharp edge. The applicator **1230** can be moved a slight distance higher than the edge **1240**, which insures that the resin **1210** goes all the way to the edge. However, as long as the extra distance is modest, the resin will not progress past the sharp edge. This behavior of the resin puddle as it is being nudged illustrates that it is quite useful and convenient to have a sharp external edge, because the hesitation which the edge causes in the spreading of liquid resin provides a sharply-defined edge of the resin-coated region and it is possible to know with quite a degree of certainty that the resin has reached all the way to the edge and no farther.

[0132] Step **4** shows that once contact of resin **1210** all the way to the sharp corner **1240** has been achieved, the applicator **12320** may be brought back down below the comer, which allows the resin drop **1210** to drift back downward under the influence of gravity. This illustration is similar to the illustration for Step **2**, except that now the resin remains in contact with the conical exterior **1220** of the nozzle **1200** all the way to the sharp comer **1240**. Shortly after this step, the applicator **1230** may be removed from contact with the resin **1210**.

[0133] Step **5** shows the situation after the applicator **1230** is removed. A layer of resin **1230** hangs downward under the influence of gravity. For low viscosity resins this layer would be rather thin, but for high viscosity resins this layer may be thicker. The layer starts at the edge where the conical exterior meets the land, and is thicker at lower elevations. In **FIG. 12**, the thickness of this layer is exaggerated for purposes of illustration.

[0134] Step **6** illustrates that if the resin is a relatively viscous heat-curing resin, as the resin becomes warm before actual curing, its viscosity decreases. This may cause the resin to creep or drip lower on the nozzle under the influence of gravity, and with the result that the layer becomes thinner especially near the tip of the nozzle. Nevertheless, the layer never completely disappears from the surfaces that have been wetted with resin, even those surfaces closest to the tip of the nozzle. Eventually, with a combination of time and temperature, the resin cures and remains in a permanent place and shape. If the resin is such that the exposed as-cured surface has a lower surface energy than the interior of the resin layer, then that will be achieved in this process.

[0135] With any coating liquid and any curing mechanism, while the coating is still liquid, it is also possible to direct a jet of clean gas at the applied liquid, blowing in a direction away from the nozzle tip, to thin the liquid layer by pushing liquid away from the nozzle tip to a place where its thickness does not matter or where it can be removed from the nozzle. It is estimated that the thickness of the cured coating at the tip of the nozzle is less than several thousandths of an inch even with the more viscous resin, and well under that dimension for the low-viscosity resin.

[0136] **FIG. 13** illustrates one embodiment of apparatus used to perform the coating operation. The apparatus provides a positioning system for an applicator that is substantially precise, stiff and free of looseness or backlash. The apparatus may be mounted on a base plate **1310** and includes a rotary table **1330**, which holds the nozzle **1320** being coated. The nozzle **1320** may be a small nozzle with a conical exterior, having an axis of symmetry **1322**, and includes a central hole or orifice **1324** which must be kept free of resin. The axis of rotation **1332** of rotary table **1330** may coincide with the axis of symmetry **1322** of nozzle **1320** and its orifice **1324**. As shown, the axis of rotation of rotary table **1330** may be vertical and the orientation of the nozzle **1320** may be vertical such that gravity pulls the resin away from the orifice **1324**, which helps to prevent the orifice **1324** from accidentally becoming filled or blocked with resin. The rotary table **1330** can be rotated by hand or upon command as needed, or it can be continuously rotated such as by a motor (not shown), at a suitably slow speed.

[**0137**] Also mounted onto base plate **1310** is a motion stage **1340**, preferably providing three axes of motion, which moves an applicator **1350** relative to nozzle **1320**. Stage **1340** may comprise three screw micrometers **1342**, **1344** and **1346** in mutually orthogonal directions. Actuators or positioners other than micrometers could also be used, as known in the fields of motion control and optics.

[**0138**] As illustrated in **FIG. 13**, the three directions of motion of the stage **1340** may be vertical and two mutually perpendicular horizontal directions. However, it also would be possible for one direction of motion to be approximately parallel to or tangent to the external surface of the axisymmetric surface being coated (i.e., when moving in the direction parallel to the slant height of a conical nozzle, the distance of the applicator from the cone surface does not change), and another direction to be perpendicular to that direction (i.e., purely toward or away from the conical surface).

[**0139**] The applicator **1350** that is moved by the stage **1340** may be a solid slender and sharp-pointed such as a pin, which is capable of moving an attached drop of resin around on the nozzle **1320**. In some circumstances it may be desirable that the applicator be a hollow tube having an interior passageway, which may be pointed or beveled like a hypodermic needle, such that liquid or resin can be delivered through its interior passageway onto the nozzle **1320**.

[**0140**] In addition to the already described apparatus, the apparatus may include a visual observation system that offers visual magnification to aid in working on small parts. This system may be a purely optical system such as a conventional microscope. The system may include an adjustable magnification (zoom) lens **1360**, an electronic camera (not visible), focusing means **1370** which may be along a vertical axis looking down at the coating apparatus, and a display monitor **1362**. Image processing software including edge recognition or contrast enhancement, as is known in the art, may be used to process an electronically acquired image, possibly in real time, to enhance visualization of the position of edges of the drop of liquid or resin, such as through contrast enhancement and edge detection.

[**0141**] It has been found that this apparatus can control the placement or position of the actual edge of a puddle of liquid or resin on a small axisymmetric work piece, sufficient to routinely and successfully coat the external conical surfaces of nozzles whose orifice diameter is at least as small as 25 microns (0.001 inch).

EXAMPLE 8

Various Other Nozzle Shapes

[**0142**] In accordance with yet another embodiment of the present invention, alternative nozzle configurations are described and illustrated. The nozzle shapes described so far, using a pre-manufactured shape that has then been coated with a low surface energy coating, have generally been frusto-conical. That is not the only possible shape, even for pre-manufactured and coated shapes.

[**0143**] First of all, the category of knife-edge orifices has already been mentioned briefly. In a knife-edge orifice, there is a transition region between the flow passageway and the extended surface, but the features at the transition region are so small compared to the orifice diameter, that the details are unimportant (such as whether the transition is flat or rounded). This embodiment may be defined as land outside diameter minus land inside diameter being less than one-tenth of the orifice diameter. Although small-diameter nozzles such as 0.003 inch diameter orifices may not afford that luxury, there could be some nozzles manufactured according to the present invention on a sufficiently large size scale, or with an appropriate manufacturing method, such that it would be possible to manufacture the orifice edge as essentially a knife-edge, such as land dimension or radius less than 1/10 orifice diameter. In such an event, a low surface energy coating may be applied on the external surface up until the knife-edge. The external surface may be conical, curved in either a concave or convex sense, or of other shape. If the external surface is other than frusto-conical, the surface tangent angle is as defined in the next paragraph.

[**0144**] It is possible that, for nozzles having a flat land, as described in Example 1, within the region where swingback is possible and nozzle design features are important, the nozzle external shape could have axisymmetric shapes other than frusto-conical, such as curved in either the concave or the convex sense. Curvature of the nozzle external surface, as one moves along the slant height, would still fall within the scope of the present invention.

[**0145**] FIGS. **14A-14C** illustrate various nozzle shape embodiments along with reference of the relevant surface tangent angle SA on each embodiment. **FIG. 14A** is a nozzle with an outwardly curving exterior surface **1410** and a flat land **1415**. The exterior surface tangent angle SA is minimized. **FIG. 14B** illustrates a nozzle with an inwardly curving exterior surface **1420** and a flat land **1425**. The exterior surface tangent angle SA is greater than in **FIG. 14A**. **FIG. 14C** is a nozzle with a relatively flat exterior surface area **1440** and a rounded land **1430**, outwardly extending from the internal passageway **1450** of the nozzle. The land **1430** in **FIG. 14C** is in the shape of a fillet. Each illustrated embodiment has a surface tangent angle greater than 90 degrees where the external shape meets the land. **FIG. 14A and** 14B illustrate the surface tangent angle for a nozzle that has a land of finite dimension and that also has an external surface which is curved in either a concave or convex sense, as opposed to being a simple frusto-conical shape.

[**0146**] It can also be realized that departures from the previously described nozzle designs are possible at a sufficiently great distance from the tip of the nozzle. To the extent that the axisymmetric low surface energy exterior is advantageous, it only exerts its advantage within a certain distance of the exit. There can be locations that are so far removed from the exit that no drop would ever be able swing up that far. Accordingly, at such places it is no longer necessary to maintain the combination of frusto-conical or other axisymmetric shape and low surface energy. It would be permissible to violate either or both of those criteria. The distance beyond which swingback could never reach, and beyond which the stated nozzle design need not be maintained, is not precisely known, but may be estimated as 0.5 inch for typical orifice and nozzle dimensions of interest for 3DP printing.

[0147] In the descriptions of the shape in previous embodiments, the nozzle has been described as having axisymmetry, which implies that the land is an annulus. While the land may be designed to be an annulus having its inner and outer circular edges being concentric with each other, it should be realized that manufacturing imperfections resulting in relative eccentricity of the two circles are permissible.

[0148] With any of these geometric alternatives, roughness could be incorporated such as is described in Examples 2,3 and 4.

[0149] In the examples so far, the low surface energy property has only been provided at the external surface such as frusto-conical surface. The land has not been coated or required to have any particular surface energy. It is possible that the land be left uncoated and have relatively high surface energy (such as greater than 50 dyne/cm) as has already been described in the earliest Examples, displaying the surface energy of the material it is made from, which may be a high surface energy exhibiting hydrophilic behavior.

[0150] Alternatively, it is also possible that the land could be manufactured to have a small surface energy similar to that of the external surface, such as by coating. For example, it is possible to coat the land with a low surface energy coated just as the external surface has been coated. The coating apparatus described in the preceding example could be used, and the sharp edge where the internal passageway meets the land could similarly be used to arrest and define the spread of the coating liquid. The usefulness depends on individual circumstances such as particular fluid being dispensed.

[0151] Alternatively, nozzles may include fillets. In some instances, the filleted ends seem to be less effective than sharp edges in arresting the spread of liquid or limiting the size of a possible puddle of dispensed liquid, or in defining the edge of a coating. However, there could be cases in which such a filleted nozzle could be useful if coated with a low surface energy coating in appropriate places. Such a nozzle could also include a flat land region on either side of the fillet, i.e., the fillet could be closer to the fluid passageway or closer to the external surface, as shown in **FIG. 14C**.

EXAMPLE 9

Alkyl Ketene Dimer

[0152] In accordance with yet another embodiment of the present invention, a coating is applied to the nozzle to increase the wetting-resistant properties of the nozzle. A type of hydrophobic surface which is hydrophobic as a result of producing a microscopically rough surface as it solidifies, is described in "Super-Water-Repellent Fractal Surfaces," by T. Onda, S. Shibuichi, N. Satoh, and K. Tsujii, in Langmuir the ACS Journal of Surfaces and Colloids, Vol. 12 no. 9, May, 1996, pages 2125-2127. The material described in this reference is alkylketene dimer (AKD) and is a naturally hydrophobic waxy substance that produces a pattern of crinkles or cracks as it solidifies from a melted state.

[0153] AKD undergoes fractal growth when it solidifies, although the mechanism has not been clarified yet. The paper compares a surface containing this fractal geometry with a surface of the same material prepared, by cutting, so as to produce an ordinary flat (non-fractal) surface. The conventional (cut) surface had a moderately good contact angle with water of 109 degrees, but, when this material was prepared so as to have a fractal surface, that surface had an extraordinarily large contact angle with water of 174 degrees. This represents extreme hydrophobicity and is far better than the contact angle for any material not having this microgeometry.

[0154] AKD could be used as a coating for nozzles instead of the fluoropolymer resin described in the previous embodiments. The hydrophobicity of this material is dependent on the presence of surface cracks resembling fractals as it solidifies from liquid. The preparation of the fractal surface in the cited article included heating the AKD material to 90 degrees C. in dry nitrogen and then letting it cool and solidify. The technique for using this material as a nozzle coating material could include depositing a thin film of this as liquid on the substrate to be coated or treated (the nozzle exterior), at a temperature of around 90 C., and then letting it cool at room temperature in the presence of dry nitrogen gas.

[0155] AKD could be applied to the exterior conical surface of a nozzle by essentially the same method and apparatus described in Example 7 for applying resin, provided that the application of the AKD is carried out at a temperature, such as 90 C., which is suitable for the melting of AKD. For example, the apparatus that holds the nozzle during application of the coating can be heated so as to melt the AKD during times when it is desired to be melted. Heat could also be applied from an external source. Solid AKD could be touched to the heated nozzle. The applicator could be heated or it does not have to be. When the nozzle is completely coated with liquid AKD in the desired places, heat could be turned off or down allowing the AKD to solidify in the desired manner.

EXAMPLE 10

Hole Drilled Through Bulk Hardened Fluoropolymer

[0156] Example 10 provides yet another embodiment of the present invention. The previous Examples provided an as-cured hydrophobic surface at the surface of a well-defined external geometry. This was achieved by manufacturing a base shape having sharp well-defined geometric features and then applying the low-surface-energy resin as a thin coating over the pre-manufactured shape. A different approach, which also provides an effective nozzle for some purposes, is to make the entire discharge region of the nozzle out of a low-surface-energy resin as a bulk material. In such a case, because a drop of resin naturally assumes a gently curved shape, it is not likely that one could achieve such sharply tapered and sharp-edged geometries as in the earlier embodiments, especially given the preference for having the final surface be an as-cured surface. Nevertheless, even assuming that most surfaces will be gently curved, it is still possible to achieve geometries that are useful for certain fluids and certain purposes.

[0157] This example depends on having a drop of resin fill certain small openings or bridge certain small gaps, therefore, the extremely low viscosity formulation PFC 1 604A from Cytonix has not been used. Instead, the more viscous heat-curable fluoroepoxy resin GH000 from Cytonix has been used. As in previous discussion, this example pertains especially to a curable resin that has its lowest surface energy at its exposed as-cured surface.

[**0158**] FIGS. **15**A-1SC illustrate the dispensing sequence of one such nozzle. FIGS. **15** illustrate the sequence of manufacturing a nozzle for dispensing a liquid through a tube **1520** having a small body of a cured resin **1510, 1530** at its end, with a hole **1540** through the cured resin.

[**0159**] The tube may be a metal tube of an inside diameter such as 0.030 inch (0.75 mm), which is such that the surface tension of the resin will be an important factor in the placement and shape of the drop of resin at the end of the tube. When liquid is placed across the end of such a small diameter tube, the liquid will wick into the tube and will have an inward meniscus at the end. Presumably at the other, hidden surface of the resin inside the tube, the resin will also have a similar meniscus that also wicks onto the wall with a concave curvature.

[**0160**] One way of manufacturing the desired final geometry is to allow a first drop **1510** of resin to assume a natural inwardly-curving shape at the end of the tube, cure it at least partially, as shown in **FIG. 15A**. Then, deposit a second drop **1530** of resin in the depression formed by the meniscus, as shown in **FIG. 15B**. The first drop **1510**, being at least partially cured, will retain its shape, and provides a resting place for the second drop **1530**, ensuring that the second drop bulges outward as desired. **FIG. 15B** illustrates the sequence after the second drop **1530** has been deposited. The second drop **1530**, assuming an appropriate volume of resin is deposited, will bulge outward by an amount depending on the volume of resin deposited, and will cure in that shape, which is a portion of a sphere. This outwardly bulging shape is what is desired and is what is desired to be of low surface energy material. **FIG. 15C** illustrates a dispensing hole **1540** in the resin **1510, 1530**.

[**0161**] The first material is not actually required to be low surface energy, and it could be any material that retains its shape after partial or full curing because its principal function is to retain its shape to prevent the second externally bulging drop, which is made of low-surface-energy material, from wicking in to the tube before it cures. If the first material is identical to the second material, it may be desirable to only partially cure the material in the first drop just enough so that the material in the first drop becomes highly viscous but still retains some ability to bond with the next drop, whereas if it were fully cured the low surface energy of its exposed surface could make it difficult for anything else, even the next layer of the same material, to stick to the first layer.

[**0162**] Thus, making the first layer out of a higher surface energy resin material might be useful simply to promote adhesion with both the tube wall and the second drop. In order to enhance adhesion of any resin to the tube, it may be advantageous to provide a geometric attachment feature such that the resin enters the attachment feature, cures and as a result the entire resin plug is mechanically trapped in its desired location at the end of the tube. The attachment feature could for example, be an internal groove or other indentation on the interior of the tube near the end where the resin plug will exist, or small holes through the tube wall, roughness on the interior surface of the tube, etc. The extent of curing of heat-curable low-surface-energy fluoroepoxy resin GH000, from Cytonix, is typically observable by color, with the resin turning brown or dark brown when cured.

[**0163**] As shown in **FIG. 15C, a** hole is created through the cured resin plug. The hole may be drilled so as to be concentric and coaxial with the tube. The hole may be made by conventional mechanical drilling, laser drilling, or any other appropriate method. The diameter of the drilled hole may typically range from 0.007 inch (177 microns) down to 0.002 inch (51 microns) or even smaller. This drilling may be performed with precautions so as to avoid disturbing the exposed as-cured surface of the resin adjacent to the hole. Laser drilling may include the use of lasers whose wavelength is in the vacuum ultraviolet range, which is believed to be especially well suited for cutting fluoropolymers.

[**0164**] FIGS. **16**A-**16**C illustrate some geometric relationships which pertain to the tangency angle at the edge of the hole of **FIG. 15C**. The shape of the drop as it is curing is a portion of a sphere having a radius of curvature. How much of a sphere and what is the radius of curvature are determined by how much resin is placed there, on the surface tension of the liquid resin, and on other details. It is assumed that there is symmetry around the longitudinal axis of the cylindrical tube and the cylindrical hole, i.e., the center of the sphere is on the axis of the cylindrical hole.

[**0165**] The angle of interest that effects the droplet breakoff is the local tangent angle of the surface SA at the edge of the nozzle exit **1610** surface, referenced to the direction of travel of the jet. This angle may be termed the surface tangent angle SA. For an ordinary hole drilled perpendicularly through a flat surface, the surface tangent angle is 90 degrees. Surface tangent angles greater than 90 degrees may be attained by the present invention. The principal variables, labeled in FIGS. **16**, are the radius of the hole r_h, and the radius of the spherical surface r_s. In all cases illustrated in FIGS. **16**, the surface tangent angle SA is at least slightly greater than 90 degrees.

[**0166**] In **FIG. 16**A, the radius of the hole r_h is much smaller than the radius of curvature of the spherical drop surface r_S. In this case, the surface tangent angle is only slightly greater than 90 degrees, perhaps only a few degrees greater than 90 degrees. In **FIG. 16**B, the hole radius r_h is about one-quarter of the spherical radius r_s, (i.e., $r_h/r_s=0.25$), and the surface tangent angle is 104 degrees, i.e., about 14 degrees beyond 90 degrees. In **FIG. 16**C, the hole radius r_h is about one-half of the spherical radius r_s, (i.e., $r_h/r_s=0.5$), and so the surface tangent angle is 120 degrees. The actual relation between the two radii and the angle is given by

$$\text{surface tangent angle}=90+\arcsin(r_h/r_s)$$

[**0167**] It can be observed that in FIGS. **16** the flow geometry for flow entering the resin plug with the hole in it includes an abrupt contraction from the inside diameter of the tube to the diameter of the hole. Such an abrupt contraction may be undesirable for at least some fluid flow purposes because it introduces into the fluid flow disturbances that may show up as irregular flow beyond the nozzle.

[**0168**] FIGS. **17**A-**17**G illustrate various embodiments that provide a smoothly-tapering interior flowpath **1705** even for this non-coating based approach, and also achieves a surface tangent angle SA significantly greater than 90 degrees just as in the previous FIGS. **16A-16C**. It involves creating, such as by machining, a nozzle body **1700** (essentially a tube) having a smoothly-tapering internal passageway **1705**. Then a drop of resin **1720** is applied to the end. A place for application of the resin, such as a recess or pocket **1710**, may be provided for this purpose. Either one-step or two-step application of resin, as before, could be used. The resin could be cured or dried to form a low-surface-energy surface. Finally, a hole **1730** is made through the resin **1720**. In **FIGS. 17C, 17F** and 17G, the diameter of the hole is shown as being essentially equal to the diameter of the lower end of the tapering flowpath in the nozzle body. This results in a smooth internal flowpath without any abrupt change in cross-sectional area. As before, the surface tangent angle at the edge of the hole is determined by the ratio of the hole radius to the radius of curvature of the spherical surface of the resin drop.

[**0169**] FIGS. **17A-17F** shows a tube whose interior is tapered near the discharge end just before the resin plug. In the case especially of small diameter orifices, such a tapering avoids the large pressure drop associated with a long length of small bore, while still not introducing major flow disturbance. It also keeps the L/D of the drilled hole within reasonable range. Most hole manufacturing methods have a limitation on length to diameter ratio of the hole, and smaller overall size of the resin drop will help to keep the L/D of the drilled hole within a reasonable range. The exterior of the pre-manufactured nozzle body in FIGS. **17A-17G** can be either straight-sided as shown in FIGS. **17A-17C**, **17G** or tapered as shown in FIGS. **17D-17F**.

[**0170**] If the diameter of the drilled hole is to be particularly small, such as 0.002 inch, or if it is desired that the surface tangent angle be particularly acute, it may be desirable for the resin region to be of particularly small diameter. Smaller size for the resin region will accentuate the curvature of the resin drop bulging outward.

[**0171**] Yet another way of making such a nozzle with a hole in it would be to cast a placeholder such as a wire into the resin and then, after curing, remove the placeholder such as by etching the wire out. The placeholder would have to be of a suitable material such as a metal wire such that it could be etched away by an acid that does not damage the cured resin.

[**0172**] For example, copper wire can be etched away by a solution of hot nitric acid without damaging the fluoroepoxy. When the wire is etched away, the hole that remains is of the diameter of the wire. Where the wire enters the drop of resin, there can be expected to be a meniscus by which the resin tries to rise up onto the surface of the wire. The dimensions of this meniscus will be of the same order of magnitude as the diameter of the wire. The shape of the meniscus may be influenced by whether the wire was simply inserted into the resin drop or whether the wire was inserted and then withdrawn slightly, because the resin follows the motion of the wire. When the wire is etched away, the meniscus will remain, and this provides a natural way of making a nozzle having a desirable kind of curvature leading to a sharp edge right at the discharge. This nozzle shape is shown in **FIG. 17G**.

[**0173**] Experiments have been conducted involving discharge of fluid from nozzles made out of fluoroepoxy, made as illustrated in FIGS. **15A-15C** and drilled with mechanical drills, in both drop-on-demand and continuous mode. The flow characteristics with nozzles of the present embodiment have been significantly better than the flow characteristics of earlier nozzles made of more conventional materials and designs. The nozzle of this embodiment, when operating with a solution of propylene glycol and water in an 80:20 proportion, remained dry in almost all operating conditions and produced good quality drops.

[**0174**] Further Discussion

[**0175**] The nozzles of the present invention could be used to dispense almost any form of fluid discharge. They could, for example, be used in dispensing a continuous jet. By virtue of their physical properties, some liquids, when dispensed intermittently, tend to immediately produce discrete drops, while other liquids dispense as a series of bulges connected by narrower strings of liquid. The nozzles of the present invention could be used in either case.

[**0176**] With microvalves, the nozzles of the present invention could be used with both drop-on-demand and line-segment modes of operation. Although the examples have been tested with solenoid-operated microvalves, the nozzles of the present invention could also be used equally well at the discharge of other types of valves and other types of dispensers. The nozzles could be used at the discharge of a piezoelectric based drop-on-demand dispenser or fluid ejection system or also with still other types of dispensers, including boiling (bubble-jet), continuous jet with deflection, and in general, any type of liquid dispenser. Among the expected benefits of wetting-resistant nozzles would be improved accuracy of drop placement and hence print quality.

[**0177**] For a piezoelectric dispenser, it may be arranged that when fluid is not being dispensed, the liquid forms a meniscus at the nozzle exit such that the meniscus bulges inward, i.e., toward the direction from which the fluid is supplied to the nozzle. This may be achieved by supplying the fluid from a fluid source that is maintained at a fluid source pressure, while the dispenser operates in a surrounding gas which is at atmospheric pressure, wherein the fluid source pressure is at lower than atmospheric pressure. This could for example be attained if the fluid source reservoir is open to atmosphere and the liquid surface level in the reservoir is at a lower elevation than the elevation of the exit of the nozzle. This will tend to draw stagnant fluid at the nozzle exit back into the flowpath until the negative pressure of the fluid supply system corresponds to the negative pressure associated with an inwardly bulging meniscus. This will encourage the last little bit of fluid at the nozzle exit, at the time of shutoff, to be drawn back into the fluid supply system, thereby making that last little bit of fluid less available for swingback. Immediately after shutoff of a dispensing or pulse train, the negative pressure and the tendency toward an inward meniscus would help remove fluid from the immediate region of the exit and this would cooperate with the nozzle design features already described, which discourage any fluid which does exist at the exit from swinging back onto the nozzle exterior, to produce a situation which is even more resistant to wetting and swingback.

[**0178**] In general, the present invention is defined by the use of a surface that is more non-wetting (lower surface energy) than the commonly known and used Teflon. The radical describing Teflon is —CF_2—. On the Zisman chart there are two listings with smaller surface energies, namely —CF_2H and —CF_3. Accordingly, a usable coating with the present invention could be any coating in which the atomic constitution at the surface is a monolayer ending in —CF_3, or in —CF_2H or a material with a high proportion of such chemical entities at the surface. Any such material is an example of a material that could be used in the current invention. Materials described in cited patents, all of which are incorporated by reference, are examples of materials that could be used.

[0179] Another example of a coating material which could be used, having a surface energy lower than that of Teflon, is the substance FC721 (also FC732) made by the 3M Company, Minneapolis, Minn. (cited in Adamson and in Contact Angles on Hydrophobic Solid Surfaces and Their Interpretation, by D. Li and A. W. Newmann, Journal of Colloid and Interface Science, vol. 148 No. 1 January 1992 p. 190-200), which is 99% perfluorooctyl methacrylate, with 1% acrylic acid.

[0180] The liquids that could be dispensed through a nozzle of the present invention include a very wide variety; essentially any liquid that has a low enough viscosity to flow through the nozzle sufficiently quickly. Specifically it includes the category of organic solvents, which includes without limitation alcohols (ethanol, methanol, isopropanol, propanol, and others), chloroform, dichloromethane, other halocarbons (including chlorocarbons, fluorocarbons, chlorofluorocarbons, hydrofluorocarbons and other halocarbons), acetone, methylene chloride, ethers (methyl tertiary butyl ether), ethyl acetate, toluene, benzene, dimethyl sulfoxide, N-methyl-2—pyrrolidone, formamide, dimethyl sulfoxide (DMSO), dioxane, acetonitrile, gamma-butyrolactone, propylene carbonate, etc. A list of possible solvents of interest is given in the CRC Handbook under “Solvents for Liquid Chromatography.”

[0181] The liquid may also include mixtures or solutions of these fluids. It can also include liquids which are any organic solvent including the above named solvents with any additive or additives dissolved in it. The additive may be either liquid or solid. Examples of additives include soluble polymers, polycaprolactone, poly-lactic acid, poly-lactic-co-glycolic acid, propylene glycol, triethyl citrate, etc. The additive could also be any Active Pharmaceutical Ingredient. The liquid may further comprise solid particles, or colloidal particles or micelles suspended in it. Nozzles of the present invention could also be used advantageously with water and with aqueous solutions including polyacrylic acid (PAA), propylene glycol, etc.

[0182] Nozzles of the present invention could be used other than for three-dimensional printing, such as for dispensing for high throughput screening of pharmacological substances. Similarly, such nozzles could be used for dispensing of liquids for biological testing, assays, etc., for medical or veterinary or other general laboratory purposes. The dispensed liquid could be blood, other bodily fluids, or reagents or diagnostic substances that are part of the testing. For example, DNA testing for biological identification, genetic research etc. involves dispensing of minute quantities of expensive substances.

[0183] Advantages of wetting-resistant nozzles for such applications include the possibility of using reduced quantities of expensive chemical or biological substances, and reduced likelihood of cross-contamination. Applications would also exist throughout the processes of manufacturing pharmaceuticals, beyond simply dispensing the completed pharmaceutical substances into dosage forms.

[0184] A filter may be mounted on each fluid line immediately before the dispenser or printhead, so as to catch particles or debris originating in any part of the fluid supply system upstream of the filter location. Such a filter may be mounted directly on the printhead.

[0185] The above description of various illustrated embodiments of the invention is not intended to be exhaustive or to limit the invention to the precise form disclosed. While specific embodiments of, and examples for, the invention are described herein for illustrative purposes, various equivalent modifications are possible within the scope of the invention, as those skilled in the relevant art will recognize. The teachings provided herein of the invention can be applied to other purposes, other than the examples described above.

[0186] The various embodiments described above can be combined to provide further embodiments. Aspects of the invention can be modified, if necessary, to employ the process, apparatuses and concepts of the various patents, applications and publications described above to provide yet further embodiments of the invention. All patents, patent applications and publications cited herein are incorporated by reference in their entirety.

[0187] These and other changes can be made to the invention in light of the above detailed description. In general, in the following claims, the terms used should not be construed to limit the invention to the specific embodiments disclosed in the specification and the claims, but should be construed to include all devices that operate under the claims to provide a method for dispensing a liquid. Accordingly, the invention is not limited by the disclosure, but instead the scope of the invention is to be determined entirely by the following claims.

I claim:

1. A nozzle for dispensing a liquid, comprising:

a dispenser including an internal flow passageway with an inlet and an outlet, wherein liquid exits the dispenser at the outlet;

a land adjoining and surrounding the outlet, the land is substantially perpendicular to a longitudinal axis of the internal flow passageway; and

a substantially axisymmetric external surface adjoining and surrounding the land, the external surface having a surface tangent angle nearest the land which is greater than 90 degrees, wherein a surface energy of the external surface is less than about 17 dyne/cm.

2. The nozzle of claim 1, wherein the substantially axisymmetric external surface is frusto-conical.

3. The nozzle of claim 1, wherein the substantially axisymmetric external surface is shaped in a concave curve.

4. The nozzle of claim 1, wherein the substantially axisymmetric external surface is shaped in a convex curve.

5. The nozzle of claim 1, wherein the internal flow passageway, the land, and the external surface are all substantially axisymmetric around a common axis.

6. The nozzle of claim 1, wherein the land has an outer edge that is substantially sharp, and wherein the outer edge is adjacent to the substantially axisymmetric external surface.

7. The nozzle of claim 1, wherein the land has an inner edge that is substantially angular, and wherein the inner edge is adjacent to the internal flow passageway.

8. The nozzle of claim 1, wherein the surface tangent angle nearest the land is greater than or approximately equal to 135 degrees.

9. The nozzle of claim 8, wherein the surface tangent angle nearest the land is greater than or approximately equal to 165 degrees.

10. The nozzle of claim 9, wherein the surface tangent angle nearest the land is greater than or approximately equal to 170 degrees.

11. The nozzle of claim 10, wherein the surface tangent angle nearest the land is greater than or approximately equal to 175 degrees.

12. The nozzle of claim 1, wherein the land has an outer circular boundary and an inner circular boundary that is substantially concentric with each other.

13. The nozzle of claim 1, wherein the land has an outer circular boundary and an inner circular boundary that is approximately concentric with each other.

14. The nozzle of claim 1, wherein the land has an outside diameter and an inside diameter, and the outside diameter divided by the inside diameter is less than or approximately equal to 5.

15. The nozzle of claim 1, wherein the land has an outside diameter and an inside diameter, and the outside diameter divided by the inside diameter is between 1.1 and 1.5.

16. The nozzle of claim 1, wherein the land has a flat land surface energy, and the land surface energy is greater than or equal to about 17 dyne/cm.

17. The nozzle of claim 1, wherein the land has a flat land surface energy, and the land surface energy is less than about 17 dyne/cm.

18. The nozzle of claim 1, wherein the internal flow passageway is tapered, having a cross-sectional flow area that becomes smaller upon progressing from the inlet to the outlet.

19. The nozzle of claim 1, wherein the internal flow passageway has an internal surface having an internal-surface surface-energy, and the internal-surface surface-energy is greater than 50 dyne/cm.

20. The nozzle of claim 1, wherein, at a distance greater than 0.5 inch away from the outlet, the external surface changes to a shape different from what it was closer to the outlet, or changes so as to have a surface energy different from what it had closer to the outlet.

21. The nozzle of claim 1, wherein the surface energy of the external surface is less than about 12 dyne/cm.

22. The nozzle of claim 1, wherein the surface energy of the external surface is less than about 8 dyne/cm.

23. The nozzle of claim 1, wherein the external surface is a coating on top of a substrate.

24. The nozzle of claim 23, wherein the substrate is made of a material selected from the group consisting of tungsten carbide, other ceramics, metals, silicon and polymers.

25. The nozzle of claim 23, wherein the coating is a substance that hardened from liquid after being applied to the nozzle.

26. The nozzle of claim 23, wherein the coating cures or hardens from a liquid by heat, by ultraviolet light, by the passage of time since the mixing of two components, or by evaporation of a solvent.

27. The nozzle of claim 23, wherein the coating has a thickness of less than about 50 microns.

28. The nozzle of claim 23, wherein the coating has a lower surface energy at its surface than it does in its interior.

29. The nozzle of claim 23, wherein the coating comprises a fluoropolymer.

30. The nozzle of claim 23, wherein the coating comprises a fluoroepoxy.

31. The nozzle of claim 23, wherein the coating has an exposed surface and the exposed surface comprises exposed terminal trifluoromethyl radicals.

32. The nozzle of claim 30, wherein a majority of the exposed surface is terminal trifluoromethyl radicals.

33. The nozzle of claim 23, wherein the coating comprises exposed CF_2H radicals.

34. The nozzle of claim 23, wherein the coating is applied by gaseous deposition or reaction.

35. The nozzle of claim 23, wherein the coating is selected from the group consisting of fluoropolymers, fluoroepoxies, fluorinated diamond-like carbon, fluorinated amorphous carbon, a siliconic polymer, poly-p-xylylene, tantalum, gold, partially fluorinated alkyl silane, perfluorinated alkane, and perfluorooctyl methacrylate.

36. The nozzle of claim 23, wherein the coating is a material that solidifies with a plurality of small cracks in its surface, whereby it becomes effectively more hydrophobic compared to the same material in a smooth-surfaced condition.

37. The nozzle of claim 36, wherein the coating is alkyl ketene dimer.

38. The nozzle of claim 1, wherein the external surface has a predetermined roughness.

39. The nozzle of claim 38, wherein the external surface has a dimensional scale of roughness that is between 1 and 50 microns.

40. The nozzle of claim 38, wherein the external surface has a total surface area and has a projected surface area, and the total surface area is more than 1.1 times the projected surface area.

41. The nozzle of claim 38, wherein the external surface is a coating on top of a substrate, and the substrate has roughness.

42. The nozzle of claim 39, wherein the substrate has roughness in a random pattern.

43. The nozzle of claim 42, wherein the roughness is produced by spark erosion.

44. The nozzle of claim 42, wherein the substrate comprises a collection of particles.

45. The nozzle of claim 41, wherein the substrate has roughness in a prescribed geometric pattern.

46. The nozzle of claim 45, wherein the pattern comprises circumferential grooves.

47. The nozzle of claim 46, wherein the grooves have a depth of about 0.001 inch and a width of about 0.001 inch.

48. The nozzle of claim 46, wherein the external surface has a projected surface area of a grooved region and the grooves in the grooved region occupy a groove area where material was removed to make the grooves, and the groove area is more than half of the projected surface area.

49. The method of claim 45, wherein the pattern comprises circumferential grooves intersected by slant-height grooves.

50. The nozzle of claim 49, wherein both the circumferential grooves and the slant-height grooves have a depth of about 0.001 inch and a width of about 0.001 inch.

51. The nozzle of claim 50, wherein the external surface has a projected surface area of a grooved region and the grooves in the grooved region occupy a groove area where material was removed to make the grooves, and the groove area is more than 60% of the projected surface area.

52. The nozzle of claim 41, wherein the coating is sufficiently thin that at least some of the substrate roughness appears as the roughness of the external surface.

53. The nozzle of claim 41, wherein the coating has a thickness of less than about 50 microns.

54. The nozzle of claim 1 further including a dispensed liquid comprising a solvent which is selected from the group consisting of ethanol, methanol, isopropanol, other alcohols, chloroform, other fluorocarbons, acetone, methylene chloride, and other organic solvents.

55. The nozzle of claim 1 further including a dispensed liquid comprising water or an aqueous solution.

56. The nozzle of claim 1, further including a dispensed liquid comprising dissolved solutes, or insoluble solid particles, or colloidal particles or micelles suspended in it.

57. The nozzle of claim 1, further including a dispensed liquid comprising an Active Pharmaceutical Ingredient.

58. The nozzle of claim 1, further including a dispensed liquid comprising blood or another bodily fluid, or a reagent or diagnostic substance, or liquid for three-dimensional printing, or liquid for high throughput screening, or liquid for performing medical or veterinary tests.

59. The nozzle of claim 1, wherein the dispenser is made by coating a substrate, which provides the shape of the substantially axisymmetric external surface, on the external surface with a coating having a surface energy less than about 17 dyne/cm.

60. A microvalve-based printhead comprising the dispenser of claim 1.

61. A piezoelectrically actuated printhead comprising the dispenser of claim 1.

62. A bubble-jet printhead comprising the dispenser of claim 1.

63. A continuous-jet printhead comprising the dispenser of claim 1.

64. A nozzle for dispensing a liquid, comprising:

a nozzle having an external surface and an internal passageway, the internal passageway having a passageway diameter, an inlet and an outlet, the passageway allowing a fluid to flow therethrough, the external surface and the internal passageway substantially axisymmetric, the external surface having a surface tangent angle nearest the outlet that is greater than 90 degrees; and

a transition region adjoining and surrounding the outlet connecting the external surface and the internal passageway, the transition region having an outer diameter and an inner diameter, wherein the outer diameter minus the inner diameter is less than one-tenth of the passageway diameter.

65. The nozzle of claim 64, further including a surface energy of the external surface wherein the surface energy is less than about 17 dyne/cm.

66. The nozzle of claim 65, wherein the surface energy of the external surface is less than about 8 dyne/cm.

67. The nozzle of claim 64, wherein the external surface is rough.

68. The nozzle of claim 64, wherein the internal flow passageway is tapered, having a cross-sectional flow area that becomes smaller upon progressing in the downstream direction.

69. A nozzle for dispensing a liquid, comprising:

a nozzle having a substantially axisymmetrical internal and an external surface, the internal surface allowing liquid to pass therethrough, the external surface having a surface energy less than about 17 dyne/cm and a surface tangent angle from the shared axis that is greater than 90 degrees.

70. The nozzle of claim 69, wherein the internal surface has an inlet and an outlet to form an internal flow passageway that conducts the liquid along a principal flow direction to the outlet.

71. The nozzle of claim 70, wherein the substantially axisymmetric external surface has a surface tangent angle nearest the outlet that is greater than 135 degrees and the external surface energy is less than about 12 dyne/cm.

72. The nozzle of claim 69, wherein the surface energy of the external surface is less than about 8 dyne/cm.

73. The nozzle of claim 69, wherein the external surface is curved.

74. The nozzle of claim 69, wherein the external surface is a portion of a sphere.

75. The nozzle of claim 69, wherein the external surface meets the flow passageway at an edge that is substantially sharp.

76. The nozzle of claim 68, wherein the internal flow passageway is gradually tapered, having a cross-sectional flow area that becomes smaller upon progressing in the downstream direction.

77. The nozzle of claim 69, wherein the external surface is formed from a drop of resin.

78. The nozzle of claim 69, wherein the nozzle is made by depositing a drop of a first resin at the end of a hollow tube, curing or partly curing the first resin to form a partly cured shape, depositing a drop of a second resin upon the partly cured shape of the first resin so as to make an outwardly curving surface, curing both resins, and making a hole through both cured resins.

79. The nozzle of claim 77, wherein the hole is made by laser drilling or mechanical drilling or by embedding a leachable placeholder and then leaching out the leachable placeholder.

80. The nozzle of claim 77, wherein the drop of second resin has a spherical shape with a spherical radius, and the hole has a hole radius, and the hole radius divided by the spherical radius is greater than 0.05.

81. A nozzle for dispensing a liquid, comprising:

an internal flow passageway along an axis that conducts a liquid along a principal flow direction toward an exit;

a fillet adjoining and surrounding the exit; and a substantially axisymmetric external surface having a surface tangent angle nearest the fillet which is greater than 90 degrees.

82. The nozzle of claim 81, wherein the fillet has a fillet surface energy and the fillet surface energy is less than about 17 dyne/cm.

83. The nozzle of claim 81, wherein the fillet has a fillet surface energy and the fillet surface energy is greater than or equal to about 17 dyne/cm.

84. The nozzle of claim 81, further comprising a transition region between the internal flow passageway and the external surface at the exit that is substantially perpendicular to the principal flow direction.

85. A method of manufacturing a nozzle for dispensing liquid, comprising:

manufacturing a nozzle having an internal flow passageway which conducts a liquid along a principal flow direction to an exit, a flat land which is substantially perpendicular to the principal flow direction, a substantially axisymmetric external surface having a surface tangent angle nearest the flat land which is greater than 90 degrees;

coating the external surface; and

curing the coating so that it has a surface energy of less than about 17 dyne/cm.

86. The method of claim 85 further comprising, coating the external surface with a liquid coating and directing a jet of gas at the coating prior to curing to thin the coating.

87. The method of claim 85 further comprising, roughening the external surface.

88. The method of claim 85 wherein the coating is gaseously applied.

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