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(54) Plasma powder processing apparatus and method

(57) Plasma processing of powder particles is performed by supplying a first gas stream, containing particle material to be processed, and a second gas stream comprising a plasma carrier gas. The first gas stream is supplied from an inlet pipe into a dielectric pipe. The dielectric pipe coaxially surrounds the inlet pipe, and extends beyond a downstream end of the inlet pipe. The second gas stream is supplied into a space between the inlet pipe and the dielectric pipe and from there into the dielectric pipe beyond a downstream end of the inlet pipe. A surface dielectric barrier plasma discharge is generated along the inner surface of the dielectric pipe at least on a part of the dielectric pipe upstream of the downstream end of the inlet pipe.

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Description

[0001] The invention relates to a plasma powder processing apparatus and method, such as a plasma powder coating apparatus and method or a plasma apparatus and method for drying droplets to form powder.

[0002] Powder is the dominant structural form of available raw materials and industry produces tons of products having a powder structure. Among them are construction materials, food and cosmetic products, composite filler materials, pharmaceuticals, catalysts, pyrotechnical materials, as well as ingredients for explosives and propellants. In general the macroscopic properties of powders are strongly influenced by their surface properties. Therefore, surface modification is an important topic in powder technology.

[0003] Plasma coating of powder particles is known for example from US 20090293675 and W02008/014607. Plasma coating of solid substrates is also known. Plasma coating typically involves supply of a coating precursor and activation (e.g. dissociation) of the precursor using plasma electrons, ions, radicals or components in excited states in the plasma. WO 2010/047593 discloses a substrate coating system that feeds a plasma carrier gas along electrodes on a dielectric body towards the substrate. WO 2010/047593 mentions the possibility of forcing the gas to flow along a parallel part of the electrode to help avoid deposition on the electrode. Other forms of plasma powder processing include formation of solid particles of submicron size formed by nucleation and growth of gaseous products of plasma, processing liquid particles that are used to form powder. Examples of processing of liquid particles are forming crystals from the liquid particles and/or charging the particles to prevent coalescence during formation and/or coating. As used herein the term particle material will be used to indicate particles as well liquid or gas components from which particles are formed, i.e. from which the matter of the particles derives. The word particle is used to refer to both solid and liquid particles, not individual molecules, ions or atoms. As used herein, "powder processing" refers to any technique to form powder from particles regardless of whether the materials used to compose particles are in the gaseous, liquid or solid state at the start of processing.

[0004] In plasma powder processing, particle material is supplied in a stream of carrier gas and optionally a coating precursor, and the particles and/or coating precursor in the stream are exposed to the reactive species produced in the plasma. Two approaches have been used exposing the stream to plasma: in situ plasma generation, in the spatial exposure region where the stream with the particles is exposed to plasma produced reactive species, or remote plasma generation, wherein plasma produced reactive species are fed from a separate plasma generation region to the exposure region.

[0005] US 20090293675 discloses in situ plasma generation. A gas stream with particles is fed into a plasma region located within a coil and a high frequency current is applied to the coil to excite the plasma. WO2008/014607 and US 5,620,743 disclose remote plasma generation.

[0006] A dielectric barrier plasma (DBP) torch is used, with electrodes on a quartz pipe to excite the plasma and a central discharge pipe to feed the plasma to a space with powder particles.

[0007] Tatsuya Moria, et al. describe powder processing in an article titled "Development of silica coating methods for powdered pigments with atmospheric pressure glow plasma", published in Thin Solid Films 316 1998, pages 89-92. Takafumi Nakajima et al also describe powder processing in an article titled "Development of powder antifoamer by atmospheric pressure glow plasma", published in Thin Solid Films 386 2001, pages 208-212.

[0008] In situ generation has the advantage that a high density of plasma produced reactive species is made possible, but it has the disadvantage that the presence of coating precursor and/or powder reduces the efficiency, stability and/or spatial uniformity of the plasma. Electronegative coating precursor gases, for example containing fluor atoms, cause a significant reduction of the plasma ionization efficiency, stability and homogeneity. Undesirable thermal filaments may be formed. Thus in situ stable and uniformly distributed non-thermal plasma generation imposes limits on the densities of coating precursor gas and powder particles. There is also a risk that the electrodes will be polluted by a coating, or by deposition of other material on the electrodes, such as the solute material in droplets. Remote plasma generation does not impose such limits, but the density of plasma produced reactive species at the location of the powder particles will be lower. In both cases there is a risk that the wall will be polluted by a coating or deposition of other material, such as droplets. Non-thermal plasma systems for coating or synthesis of powders suffer from three main problems, viz. low coating or growth rates, thermal damage to reactor or powder products, and pollution of the reactor wall surface.

[0009] It is an object to provide a plasma powder processing apparatus wherein pollution of a reaction wall surface is counteracted. Thereto, according to an aspect, a plasma powder processing apparatus according to claim 1 is provided. Herein a first gas stream, with particle material is supplied to a reaction chamber through a particle inlet pipe. Plasma produced reactive species are supplied in a second gas stream, from a space between the inlet pipe and a dielectric pipe that surrounds the inlet pipe. Electrode structures are used that face each other from an inner and outer radial position respectively, with at least part of a radial extent of the dielectric pipe between first and second electrode structures. The electrode structures are provided to generate a surface dielectric barrier discharge (SDBD) plasma on the inner surface of the dielectric pipe along a majority of its entire circumference, within the space between the inlet pipe and a dielectric pipe. In an embodiment, the majority forms substantially the entire circumference. To generate the surface dielectric barrier discharge plasma, the electrode structures comprise an inner electrode structure with conductor lines that are mutually separated by non-conductive spaces. The conductor lines may be realized as conductor lines on the inner surface of the dielectric pipe for example, exposed to the second gas stream, or embedded in dielectric material that may be part of the dielectric pipe.

[0010] The second gas stream, which is used to supply the plasma produced reactive species at least on a majority of the circumference, surrounds the first gas stream. It mixes with the first gas stream to process the particles in a mixing region, keeping the first gas stream off the wall at least for the limited distance. This allows chemicals that have become reactive upon mixing time to return to a passive state before reaching the wall. As an additional advantage the coating and/or synthesis/growth rate of powder particles is improved. The particles may be coated for example, using a first gas stream that contains coating precursor. In another embodiment the plasma produced reactive species may be used to nucleate and promote growth to form sub-micrometer sized powder particles as a result of reaction with gases in the first gas stream or to synthesize powder particles by evaporation and electrical charging of liquid particles in the first gas stream.

[0011] By means of plasma generation on the inner surface of the dielectric pipe before the downstream end of the inlet pipe a high density of plasma produced reactive species can be produced and mixed with the particles in the first gas stream immediately downstream of the inlet pipe. In an embodiment the conductor lines cover an area of the inner surface of the dielectric pipe that extends downstream of the downstream end of the inlet pipe (by "covering an area" it is meant that the conductors act to generate a plasma in the area). Thus additional plasma and plasma produced reactive species can be generated also along the wall of the reactor chamber, after the point where the first gas stream with the particles enters in contact with the second gas stream with the plasma produced reactive species. More generally the conductor lines may cover an area along the entire circumference of the inner surface of the dielectric pipe where only the second gas stream flows, substantially unmixed with the first gas stream, between the inlet pipe and the dielectric pipe and/or beyond the downstream end of the inlet pipe.

[0012] In an embodiment the downstream end of the particle material stream inlet pipe lies in a radial plane transverse to the axis of the reaction chamber. Thus the surface area of the downstream end is minimized. In an embodiment the first electrode structure comprises a liquid flow channel configured to guide a flow of liquid along the outer surface of the dielectric pipe. The liquid may be used to cool the electrode structure.

[0013] In an embodiment, the inner surface of the dielectric pipe is covered by means of conductor lines provided on the inner surface of the dielectric pipe. In another embodiment the conductor lines may be embedded in the dielectric pipe. In another embodiment the inner surface of the dielectric may be covered by conductor lines provided on an outer surface of the particle inlet pipe, extending radially to contact the inner surface of the dielectric pipe or to reach close to the inner surface, without contact. Each of these solutions makes it possible to generate a high electric field strength at the dielectric inner surface of the dielectric pipe for generating a surface dielectric barrier discharge plasma. The conductor lines may extend axially, or the conductor lines may be successive windings of a spiral for example.

[0014] In an embodiment the voltage applied between the electrode structures inside and outside the dielectric pipe has both a DC component and an AC component. This may be used to increase the number of ions in the second gas stream and give it a net electric charge by driving ions from the inner surface of the dielectric pipe.

[0015] In an embodiment an electrode structure is provided in the inner pipe to generate an additional electrical discharge plasma in the inlet pipe, upstream from the downstream end of the inlet pipe. This electrode structure may be a dielectric barrier electrode structure, to generate a dielectric barrier discharge plasma or it may comprise a corona electrode to generate a corona discharge plasma. Plasma generation in the first gas stream may help to prevent aggregation of the powder particles. Use of dielectric barrier discharge plasma generation has the advantage that it can more easily be realized within the limited space of the inner pipe.

[0016] In an embodiment, net electrical charging of the first gas stream is provided for. That is, an electrode within the inner pipe is used and a generator is provided that generates a voltage between that electrode and a counter electrode outside the inner pipe, the voltage having an AC component and a non-zero DC component. The polarity of the net charge of the first gas stream may be selected in correspondence with that of the plasma generated on the inner surface of the dielectric reactor pipe. When the electrical discharges in the first and second gas stream are selected to provide for net charging of the first and second gas stream with mutually opposite polarity, this can be used to promote mixing. When the electrical discharges in the first and second gas stream are selected to provide for charging of the first and second gas stream with the same polarity, this can be used to extend the distance from the downstream end of the inlet pipe where the first gas stream does not reach the inner surface of the dielectric pipe, and hence the area that can be covered by the conductor lines covering the dielectric pipe. Both effects, improved mixing and electrostatic repulsion of charged powder particles from the SDBD plasma on the dielectric pipe 14 are improved when the net charge provided by the SDBD plasma to the mixing region of the first and second gas stream, exceeds the net charge provided by the electrical discharge plasma to the first gas stream in the inlet pipe.

[0017] In an embodiment a conical flow shaper in the inlet pipe is used, that extends beyond the downstream end of the inlet pipe with tapering diameter. This provides for a counter flow that recirculates powder particles in the reaction chamber to the downstream end of the inlet pipe where the plasma is supplied. In a further embodiment the flow shaper may be mounted on a vibrator. Thus powder particles that settle on the flow shaper may be shook off.

[0018] In an embodiment the apparatus comprises a conical gas flow director within the inlet pipe. This may be used to concentrate the first gas stream near the wall of the inlet pipe, to increase coating efficiency.

[0019] In an embodiment, the inlet pipe and the dielectric may have a circular cross-section. This improves homogeneity of mixing.

[0020] A method of plasma processing of powder particles is provided wherein coaxial pipes are used to supply first and second gas stream, with a plasma discharge structure on the wall of the outer pipe. The first gas stream is supplied in the inner pipe and the second gas stream is supplied between the pipes. In an embodiment the first gas stream contains coating precursor gas. An embodiment of the method comprises switching between a coating phase and a cleaning phase, powder particles and coating precursor being supplied in the coating phase, the supply of powder and coating precursor in the first gas stream being interrupted in the cleaning phase, and plasma generation using the electrode structure being continued in the coating phase and the cleaning phase.

[0021] Other advantageous embodiments according to the invention are described in the following claims.

[0022] These and other objects and advantages will become apparent from a description of exemplary embodiments, with reference to the accompanying figures in which

Fig. 1 shows a schematic cross sectional view of a plasma powder coating apparatus

Fig.1a shows a partial cross-section of an embodiment

Fig. 2a-e show transverse cross-sections of embodiments of the plasma powder coating apparatus

Fig. 3 illustrates gas regions in the plasma powder coating apparatus

Fig. 4 shows a plasma powder coating apparatus with auxiliary discharge electrodes

Fig. 5 shows a plasma powder coating apparatus with a flow shaper

Fig. 6 shows a plasma powder coating apparatus with a flow shaper

Fig. 7 shows a plasma powder coating apparatus for deposition of activated droplets.

[0023] The figures are merely schematic views of embodiments. In the figures, the same reference numbers refer to equal or corresponding parts.

Detailed description of exemplary embodiments

[0024] Figure 1 shows a schematic longitudinal cross section of a plasma powder coating apparatus. The apparatus comprises a base portion 10, an inlet pipe 12, a non-conductive dielectric reactor pipe 14, and a plasma carrier gas input 16. Electrode structures 18a, b are located on part of the outer and inner walls of dielectric reactor pipe 14 respectively. Dielectric reactor pipe 14 is mounted on base portion 10. Inlet pipe 12 extends through base portion 10 coaxially with dielectric reactor pipe 14 within dielectric reactor pipe 14, over part of the length of dielectric reactor pipe 14. The figure shows a cross section of the apparatus with a virtual plane through the common axis of inlet pipe 12 and dielectric reactor pipe 14.

[0025] Plasma carrier gas input 16 feeds into the space between inlet pipe 12 and dielectric reactor pipe 14, along the entire circumference of inlet pipe 12. A first electrode structure 18a is located on the outer surface of dielectric reactor pipe 14 and a second electrode structure 18b is located on the inner surface of dielectric reactor pipe 14. First electrode structure 18a may cover the entire circumference of dielectric reactor pipe 14 over the entire height of first electrode structure 18a. In another embodiment at least a majority is covered, that is, at least half the circumference. Preferably substantially the entire circumference is covered, possibly except near corners in the circumference. Where the second electrode structure 18b covers the pipe, second electrode structure 18b comprises conductor lines on the inner surface of dielectric reactor pipe 14, separated by inner wall portions that are not covered by any conductor. As used herein, a surface part is covered by a surface dielectric barrier discharge electrode structure when the electrode structure provides for an electric field on the surface to generate a surface dielectric barrier discharge plasma, no matter whether the electrode structure is in contact with the surface part or near to it everywhere on the surface part.

[0026] Figure 2a shows a transverse (radial) cross-section of the apparatus, through a plane perpendicular to the common axis of inlet pipe 12 and dielectric reactor pipe 14. The conductor lines extend perpendicularly to this plane. Second electrode structure (reference 18b not used) comprises conductor lines 20 (only one labelled), mutually separated by non-conductive spaces on the inner surface of dielectric reactor pipe 14. Figure 2d shows an alternative wherein conductor lines 20 are embedded in dielectric reactor pipe 14. This implies that a higher electric field is needed to generate the plasma, but it may have the advantage that conductor lines 20 are not exposed to erosion and that a flatter inner surface is realized, on which particles will less easily stick. This structure may be realized for example by defining the conductor lines on an inner surface and applying a dielectric layer over the inner surface and the conductor lines, or by starting from conductor lines 20 as a skeleton and forming the entire dielectric reactor pipe 14 around this skeleton.

[0027] Figure 2b shows a cross section like that of figure 2a, wherein the second electrode structure comprises conductor lines 22 that are in radial contact with inlet pipe 12. Conductor lines 20 may be provided as ribs on inlet pipe 12, extending toward dielectric pipe 14, contacting dielectric pipe 14. Figure 2c shows a cross section like that of figure 2a, wherein the conductor lines 24 are provided on inlet pipe 12, without extending into contact with dielectric pipe 14. In an alternative similar to the case of figure 2d, the conductor lines 24 may be embedded in inlet pipe 12. In each case, the conductor lines cover an area of the inner surface of dielectric pipe 14 in the sense that they provide for electric field on the inner surface to generate a surface dielectric plasma discharge. Inlet pipe 12 may be conductive or non-conductive. Conductor lines 20, 22, 24 in figures 2a-e and the spaces between these conductor lines are not drawn to scale. Nor is the number of conductor lines representative.

[0028] As will be appreciated, it is easier to cover an area of the inner surface of dielectric pipe that extends beyond the downstream end of inlet pipe 12 by means of conductor lines 20 on the inner surface of dielectric pipe 14. Optionally such an area may be covered by means of ribs (not shown) on inlet pipe 12 that extend beyond the end of inlet pipe 12 itself, or in other words with an inlet pipe that has a closed circumference up to its end and an interrupted circumference beyond its end to provide for mixing of the gas streams. However, the implementation with conductor lines 20 on the inner surface of dielectric pipe is easier to realize. Moreover, conductor lines 20 on the dielectric pipe 14 preferentially have a small thickness in a range of 1-100 micrometer for example. In this way optimum gas flow conditions to avoid deposition of solid or gas materials on the dielectric pipe 14 can be obtained.

[0029] In the embodiment of figure 1, conductor lines 20 extend axially along the inner surface of dielectric reactor pipe 14. Conductor lines 20 may be coupled in common to a terminal on base portion 10. Inlet pipe 12 and dielectric reactor pipe 14 have a circular cross-section, completely surrounding an inner space of the pipes in the cross-section. Conductor lines 20 are provided at positions along the entire inner circumference shown in the cross-section of figure 2, spaced from each other at the same distance along the entire inner circumference. In an embodiment conductor lines 20 made of Pt, Pd, Ag, Au or a mixture may be used. This provides for high abrasion resistance and chemical inertness. Depending on the agressiveness of the environment other materials may also be used.

[0030] Conductor lines 20 may have a thickness in the radial direction of dielectric reactor pipe 14 in a range of 1-100 micrometer, 10 micrometer for example. Conductor lines 20 with a width in the circumferential direction of dielectric reactor pipe 14 in a range of 0.5 to 2 millimetre may be used for example, 1.5 millimetre for example, with non-conductive spaces of between 2 to 10 millimetre for example, a spacing of 5 millimetre for example. In an embodiment conductor lines 20 extend 50 millimetres beyond the downstream end of inlet pipe 12. In other embodiments conductor lines 20 extend between 10 and 200 millimetre beyond the downstream end of inlet pipe 12 for example.

[0031] The first and second electrode structures 18a, b extend from within a first region on dielectric reactor pipe 14 where inlet pipe 12 extends within dielectric reactor pipe 14 to within a second region of dielectric reactor pipe 14 to which inlet pipe does not extend. In particular, conductor lines 20 extend axially from within the first region to within the second region. In other words, the end of inlet pipe 12 lies within the range of axial positions that is covered by the conductor lines of second electrode structure 18b. Thus plasma generation over a large area is provided for, including plasma generation upstream of the end of inlet pipe, to provide for a high density of plasma products at the end of inlet pipe, and beyond the end, to replenish plasma product density beyond the end. In an alternative embodiment, illustrated as a half cross-section in figure 1a, the area covered by the conductor lines of second electrode structure 18a does not extend beyond the end of inlet pipe 12. This may reduce the risk of fouling. The inner wall of the dielectric pipe 14 and the inner and outer wall of the inlet pipe 12 have continuous rotation symmetry under rotation around the axis of the pipes, at least at the height where inlet pipe 10 ends and conductor lines 20 are provided in a rotationally symmetric manner, conductor lines 20 repeating at regular intervals.

[0032] In an embodiment dielectric reactor pipe 14 is made of Alumina (A12O3). The distance between the inner surface of dielectric reactor pipe 14 and the outer surface of inlet pipe 12 may have a value in a range of 0.2 to 2 millimetres for example, 0.5 millimetres for example.

[0033] In operation a first gas stream with a carrier gas carrying powder particles and a coating precursor is fed through inlet pipe 12. The carrier gas may be Argon or Nitrogen (N2) for example and an example of a precursor is fluorocarbon (C3F6 or C4F8 for example). But other materials may be used. A plasma carrier gas is fed to plasma carrier gas input 16 and from there to the space between inlet pipe 12 and dielectric reactor pipe 14. This gives rise to a second gas stream between dielectric reactor pipe 14 and inlet pipe 12 and beyond the end of inlet pipe 12. Gasses at atmospheric pressure may be used (1000 mbar). Other pressures may be used, for example pressures in a range of 100 - 2000 mbar.

[0034] An electric field is applied between first and second electrode structure 18a,b to excite a plasma. The plasma is generated using the dielectric barrier plasma generation process, wherein electric fields lines that pass from second electrode structure 18b through the space adjacent dielectric reactor pipe 14 and from there through dielectric reactor pipe 14 to first electrode structure 18a give rise to the plasma. In the embodiment of figure 1, plasma generation occurs both at the wall of dielectric reactor pipe 14 where inlet pipe 12 runs within dielectric reactor pipe 14 and beyond the end of inlet pipe 12.

[0035] The flow of plasma carrier gas along the inner wall of dielectric reactor pipe 14 creates a separation between the first gas stream and the inner wall of dielectric reactor pipe 14 along a part of the inner wall of dielectric reactor pipe 14 that extends beyond the end of inlet pipe 12.

[0036] Figure 3 illustrates separation. Dielectric reactor pipe 14 and the end of inlet pipe 12 are shown in a longitudinal cross-section. A number of regions can be distinguished: a first region 31 where the first gas stream with the powder particles flows unmixed with the second gas stream, a second region 32 where the second gas stream flows unmixed with the first gas stream and a mixing region 35, 37, 39 where the first and second gas stream mix. Mixing region 35, 37, 39 reaches the inner wall of dielectric reactor pipe 14 at a distance from the end of inlet pipe 12. The second electrode structure 18b ends at a smaller distance from the end of inlet pipe 12. The illustrated pattern of regions extends circumferentially in a rotationally symmetric way along the inner wall of dielectric reactor pipe 14.

[0037] Within mixing region 35, 37, 39 a first sub-region 35 can be distinguished wherein reactive products produced by the plasma in mixing region 35, 37, 39 are able to form a coating, and a second sub-region 37 where the reactive products have made a transition to a stable (non-reactive) state.

[0038] Although an example has been described wherein mixing region 35 is used for coating formation on existing powder material, it should be appreciated that mixing region 35 may be used for other types of power processing. For example it may be used for synthesis of powder from gas phase reactions between the first gas stream and the second (plasma activated) gas stream or for synthesis of powder from mixing, electrical charging, evaporation or chemical reaction of liquid droplets in the first gas stream with plasma activated particles in the second gas stream or for synthesis of powder from combined effects of gas-solid, gas-gas or gas-liquid reactions.

[0039] Of course, there is no sharp boundary between these sub-regions. To emphasize this, a transition region 39 has been shown between the two. A point to note is that only the second sub-region 37 extends beyond the distance at which mixing region 35, 37, 39 comes into contact with the inner wall of dielectric reactor pipe 14.

[0040] Within first sub-region 35 and transition region 39, mixing region 35, 37, 39 has no contact with the inner wall of dielectric reactor pipe 14. In this way fouling of the inner wall of dielectric reactor pipe 14 due to reactive products produced by the plasma is counteracted. The distance over which second electrode structure 18b extends axially beyond the downstream end of inlet pipe is chosen so that it ends before the first gas stream comes into contact with the inner surface of dielectric reactor pipe 14. In this way, supply of plasma produced reactive species that could lead to coating forming reactions at the inner surface is prevented. In the embodiment of figure 1a the second electrode structure 18b ends before or at the downstream end of inlet pipe 12. Under some process conditions this may provide for a sufficient amount of plasma produced reactive species, at the same reducing the risk of fouling of the inner surface by avoiding the surface dielectric plasma generation beyond the end of inlet pipe 12. Because at least part of the plasma is generated in a region without coating precursor gas and powder particles, the coating precursor gas and powder particles have less influence on the plasma ionization efficiency. As a consequence, the coating and/or synthesis/growth rate of powder particles is improved.

[0041] The first and second gas stream may have substantially equal flow speed at the end of inlet pipe 12. This helps to maximize the distance from the end of inlet pipe 12 to where the mixing region reaches the wall. Of course, equal flow speeds may correspond to different flow volumes or different mass flows.

[0042] An example has been shown wherein the second gas flow with plasma products is used to prevent fouling in a coating process, by preventing still reactive components from reaching the wall. When solid particles are supplied the particles by themselves typically do not present a fouling risk: the coating chemicals form the problem. In an embodiment, liquid particles are supplied. These may give rise to a fouling problem by themselves if they are deposited on the inner surface of dielectric reactor pipe 14 before solidification. In this case, the ions from the second gas stream from the space between inlet pipe 12 and dielectric reactor pipe 14 may be used to charge in particular those liquid particles that approach the wall, to keep them off the inner surface.

[0043] Although a specific embodiment of the apparatus has been shown by way of example, it should be emphasized that various modifications are possible. For example instead of axially extending conductor lines 20, one or more spiralling conductor lines may be used, that run along a spiral curve on the inner wall of dielectric reactor pipe 14, with a non-conductive spacing between successive revolutions of the spiral or spirals. Instead of an inner pipe 12 and a dielectric reactor pipe with inner walls that have a circular radial cross section, other closed cross sections may be used, for an oval cross-section such as an elliptical cross-section, or a polygonal cross-section, for example a rectangular cross section. In an embodiment inlet pipe 12 and dielectric reactor pipe 14 provide for a plurality of sections, successively along the circumference, where both are planar and parallel to each other. Thus homogeneous plasma generation conditions can be realized. The cross-section need not remain the same as a function of position along the axial direction of the pipes.

[0044] Fig. 2e shows an embodiment wherein both inlet pipe 12 and dielectric reactor pipe 14 have an elongated rectangular cross section. One example of a length/width ratio of the rectangle is shown, but it should be understood that other ratios may be used. The cross-section of inlet pipe 12 may have a length/width ratio of at least 5:1 and more preferably 10:1 for example. When a cross-section of narrow width is used electrode structures 18a,b on the narrow side of the rectangle may be omitted, as shown in the figure. In this case the second gas stream at the narrow stream still keeps the first gas stream from the inner surface of dielectric reactor pipe 14, but no plasma is generated on the narrow side. If the width is small this does not lead to a great loss. Although perfectly rectangular pipes are shown, it should be appreciated that deviation from a perfect rectangle, such as rounder corners, for example of inlet pipe 12 may be used.

[0045] The use of an inlet pipe 12 with a cross-section of narrow width has the advantage that a greater fraction of the first gas stream from inlet pipe 12 reaches the mixing region, so that higher efficiency processing is possible. In an embodiment, the inner width of the cross-section of inlet pipe 12 is less than four times the distance from inlet pipe 12 to dielectric reactor pipe 14, or even no more than two times that distance. The rectangular shape means that it is easy to use an array of parallel reactors. For example a series op parallel dielectric reactor pipes 14 of rectangular cross-section may be used, with the longest sides of the cross-sections facing those of adjacent dielectric reactor pipes 14, with first electrode structures 18a in between, and second electrode structures 18b and inlet pipes 12 inside each of the dielectric reactor pipes 14. Thus a very compact high volume plasma processing apparatus may be realized.

[0046] Although an embodiment has been shown wherein axial flow is used along the entire electrode structures 18a,b, it should be appreciated that other solutions are possible. For example, part of the electrode structures 18a,b upstream of the end of inlet pipe 12 may extend radially from the outer wall of inlet pipe 12 in a flow channel part that feeds into the space between inlet pipe 12 and dielectric reactor pipe 14.

[0047] Although an embodiment has been shown wherein the downstream end of inlet pipe 12 lies in a plane perpendicular to the axis of the pipes, it should be appreciated that alternatively the end may lie in a plane that makes a non-ninety degree angle with the axis, or not even in a plane at all. In this case, what has been said for the axial extent of the electrode structures applies at each position along the circumference of dielectric pipe 14 relative to the axial location of the end of inlet pipe 12 at that position along the circumference. For each position along the circumference, the electrode structure may extend upstream from the axial location or the inlet pipe end corresponding to that position to downstream from the axial location.

[0048] Although an embodiment has been shown wherein the electrode structures cover the entire circumference of dielectric reactor pipe 14 between first and second axial positions upstream and downstream of the end of inlet pipe 12, it should be appreciated that less circumferential coverage may suffice, as long as at least a substantial part is covered. As used herein, substantial coverage means that the size of any uncovered area is so small that gas movement ensures that the entire circumference is still effectively covered by plasma. Similarly, although an embodiment has been shown wherein there is a gap between inlet pipe 12 and dielectric reactor pipe along their entire circumference, allowing unimpeded axial gas flow along the entire circumference, it should be appreciated that a gap need not be present everywhere. For example, spacers may be present at some positions along the circumference, as long as there is a gap substantially everywhere in the sense that the areas where there are no gaps are so small that gas movement ensures that there is effective axial gas flow along the entire circumference.

[0049] Further structures may be present at the input of inlet pipe 12 and at the output of dielectric reactor pipe 14. For example, an additional inlet pipe (not shown) may be provided connected to inlet pipe 12. A series connection of a plurality of structures may be used, each comprising a base portion 10, an inlet pipe 12, a dielectric reactor pipe 14, and a plasma carrier gas input 16 and electrode structures 18a, b on part of the inner and outer walls, the dielectric reactor pipe 14 of each except the last coating structure feeding into, or forming, the inlet pipe 12 of the next coating structure, optionally via an intermediate pipe (not shown). Optionally additional coating precursor may be injected into the gas stream between successive coating structures and/or into the inlet pipes. Thus multiple coating layers may be deposited. Each layer may have the same composition, but alternatively layers of mutually different composition may be deposited by injecting mutually different coating precursors.

[0050] In an embodiment first electrode structure 18a comprises a conductive liquid electrode structure, such as a flow channel around dielectric reactor pipe 14 with an inlet and an outlet for conductive liquid and electrical connections for applying an electric potential (e.g. ground potential) to the liquid. In operation, conductive liquid may be passed through the flow channel and the electric potential may be applied to the conductive liquid. The conductive liquid may be re-circulated back from the outlet to the inlet and cooled during re-circulation. Alternatively, the first electrode structure 18a may comprise a layer of solid conductor material on the outer wall of dielectric reactor pipe 14. The layer of solid conductor material may be connected to a terminal for applying an electric potential. A cooling or temperature conditioning circuit may be provided, thermally coupled to the layer of solid conductor material, for cooling or temperature controlling with a flow of temperature conditioning fluid, which need not be conductive.

[0051] In an embodiment operation of the apparatus comprises switching between a coating phase and a cleaning phase. The coating phase corresponds to the operation described in the preceding. In the cleaning phase the supply of powder and coating precursor is interrupted. Air or different N2-02 mixtures or Ar-02 mixtures may be as plasma carrier gas for example. Plasma generation using electrode structures 18a,b is continued in the cleaning phase. Thus a highly reactive plasma sheath is produced, with which fouling of the inner wall of dielectric reactor pipe 14 is removed.

[0052] This type of cleaning phase presents only a minor interruption of operation, for which the apparatus need not be disassembled.

[0053] Figure 4 shows an embodiment of the apparatus wherein a further discharge electrode structure 40 is provided in inlet pipe 12 upstream from the end of inlet pipe 12. A counter electrode 40b is provided on an outer wall of inlet pipe 12, facing further discharge electrode structure 40. A first generator 42 electrically connected to the first and second electrode structures 18a, 18b is provided. In the illustrated embodiment the first electrode structure 18a comprises a liquid channel 43, for supplying a flow of conductive liquid that acts as electrode. In this case one of the terminals of first generator 42 may end in liquid channel 43 to contact the conductive liquid during operation, the other terminal being connected to second electrode structure 18b. By way of illustration a connection through base 10 is shown. Base 10 may be electrically isolating.

[0054] Furthermore, a second generator 44 coupled to further discharge electrode structure 40, and counter electrode 40b is provided. First and second generator 42, 44 may be electrically coupled to define the potential levels of their terminals relative to each other. Selected terminals of the first and second generator 42, 44 may have equal potential.

[0055] Further discharge electrode structure 40, 40b may have a surface dielectric barrier discharge electrode configuration, like second electrode structure 18b, covering substantially the entire circumference of the inner wall of inlet pipe 12. In this case at least a section of inlet pipe 12 is made of non-conductive dielectric material and further discharge electrode structure 40 may comprise one or more conductor lines on a dielectric wall, separated by non-conductive spaces. In this embodiment counter electrode 40b may be provided on the outer wall of inlet pipe 12, facing further discharge electrode structure 40. Although an embodiment has been shown wherein two generators are used to drive the first and second electrode structure 18a,b and the further electrode structure 40 and its counter electrode 40b it should be appreciated that under some circumstances the same generator may be used for both.

[0056] In operation first generator 42 applies a voltage that has both an AC and a DC component between first and second electrode structures 18a,b. Edges in the AC component, for example square shaped or pulsed voltage waveforms, help to create the plasma. The DC component helps to move ions off the inner surface of dielectric reactor pipe 14, and imparts a charge to the second gas stream. The voltage with AC and DC components may be realized by means of successive voltage pulses of one polarity. Alternatively, it may be realized by adding a DC voltage and an AC voltage signal. In one embodiment a DC voltage between 0.5-1kV and an AC voltage of 4-8kV was used. The polarity of the charge is determined by the polarity of the DC component. When the waveform of the AC voltage comprises short alternating pulses, a lower DC voltage, for example 10-100 Volt may be used. Also the DC component may be realized by means of alternating pulses with a difference between the amplitude of the positive and the negative pulses.

[0057] Second generator 44 applies an electric voltage between the further electrode structure 40 and its counter electrode 40b. This electric voltage also has both an AC and a DC component. The resulting discharge produces charges that are captured by the particles in the first gas stream, which prevents coalescence of liquid particles for example.

[0058] In another embodiment further electrode structure 40 may be a corona discharge electrode. In this case counter electrode is placed at a greater distance from further electrode structure 40: it may be formed by base portion 10 for example. The corona discharge electrode comprises a conductive structure with a sharp end, which results in high electric field strength at the sharp end. As used herein, a sharp end is an end that has a shape that results in locally increased electric field strength. The electrode may have the form of a conductive ring, or further pipe within inlet pipe 12, the ring or further pipe ending in a sharp end. In a further embodiment the sharp end may be provided with sharp teeth. In another embodiment the corona discharge electrode may comprise a pointed rod in inlet pipe 12. The use of a surface dielectric barrier discharge electrode configuration for the further electrode structure 40 makes it possible to use a narrower inlet pipe 12, or leave more space for other structures than for a simpler corona discharge structure. Also, it may lead to less disturbance of gas flow.

[0059] In one embodiment a voltage of 10kV was used for the corona discharge. In an embodiment, a negative potential is applied to corona discharge electrode 40 so as to charge the powder particles with negative polarity. Negative charging is more easily achieved.

[0060] Charging of any of the first and second gas stream is realized by using an electrode voltage with a DC component. The DC component drives same polarity charges away from the electrode, into the gas stream. Charging of any of the first and second gas stream may help to reduce particle aggregation and deposition on the walls. Charging may also assist in filtering using an electrostatic filter (not shown) downstream from the reaction chamber.

[0061] Various combinations of charge polarity of the first and second gas stream may be used, even if there is no need to prevent coalescence. In an embodiment the first gas stream from inlet pipe 10 and the second gas stream from the space between inlet pipe 12 and dielectric reactor pipe 14 are charged with opposite polarity. The electrostatic force between particles in the two gas streams charged with mutually opposite polarity improves fast mixing beyond the end of inlet pipe 12. In another embodiment the first gas stream from inlet pipe 12 and the inner surface of the second gas stream from the space between inlet pipe 12 and dielectric reactor pipe 14 are charged with the same polarity. This keeps the first gas stream off the inner surface of dielectric reactor pipe 14 for a longer distance beyond the end of inlet pipe 12. This makes it possible to use a longer second electrode structure 18b, allowing for a longer mixing area.

[0062] Both effects, improved mixing and electrostatic repulsion of charged powder particles from the SDBD plasma on the dielectric pipe 14 can be obtained in combination when the net charge provided by the SDBD plasma to the mixing region of the first and second gas stream, exceeds the net charge provided by the electrical discharge plasma to the first gas stream in the inlet pipe.

[0063] Further discharge electrode structure 40 may be provided upstream of first and second electrode structure 18a,b as shown. This facilitates separate driving without undesirable plasma formation between the electrode structures. In another embodiment the axial position of further discharge electrode structure 40 may overlap with that of first and second electrode structure 18a, b, and it may extend substantially to the end of inlet pipe 12. In this way it is easier to provide a charged first gas stream beyond the end of inlet pipe 12.

[0064] Figure 5 shows an embodiment wherein a flow shaper 50 and a vibrator 52 are used. Flow shaper 50 is mounted on vibrator 52. Flow shaper 50 is made of gas blocking material. It has a conical shape which narrows down from a widest diameter at an axial position upstream of the end of inlet pipe 12, or at the end of inlet pipe 12 to a smallest diameter further downstream.

[0065] In operation flow shaper 50 has the effect of creating a counter flow along the surface of flow shaper, which recirculates powder particles to the axial position where the plasma is introduced from the space between inlet pipe 12 and dielectric reactor pipe 14. Thus more coating may be applied. In an embodiment the gas flow is directed upward, against the direction of gravity, so that the counter flow of powder particles is created under influence of gravity, due to decreased flow speed higher up. Vibrator 52 causes a vibrating motion of flow shaper 50, to shake of powder from flow shaper 50.

[0066] Furthermore, as shown in figure 5, the device may comprise an inlet for gas 55, a gas distributing ring 54 and a particle diffuser 53 made of a porous glass filter. Inlet for gas 55 is coupled to gas distributing ring 54 and from there to the inner space of inlet pipe 12 via particle diffuser 53. Particles are supplied to particle diffuser 53 to create a fluidized bed of powder particles in the reactor.

[0067] Figure 6 shows an embodiment wherein a conical gas flow shaper 69 is used, located in inlet pipe 12 upstream of the end of inlet pipe 12. Furthermore a solvent inlet and outlet 62a, b, a Collison nebulizer gas inlet 63, a Collison nebulizer spray outlet 60 and an additional gas flow 61 are shown.

[0068] Conical gas flow director 69 narrows down in the gas flow direction in inlet pipe 12. Between the inner wall of inlet pipe 12 and conical gas flow director 69 a flow space for gas flow is formed that extends from an outer radius defined by inlet pipe 12 to an inner radius defined by conical gas flow director 69. The width of this flow space narrows towards the end of inlet pipe, forcing the first gas stream in inlet pipe 12 to concentrate towards the wall of inlet pipe 12.

[0069] In operation conical gas flow director 69 serves to concentrate the stream of droplets or powder particles in a ring shaped space adjacent the radial distance where the plasma is formed on the wall of dielectric reactor pipe 14 mixes with the first gas stream with powder particles. This provides for higher efficiency of mixing of the first gas stream with droplets or powder with plasma activated gas.

[0070] In an embodiment, a narrowest point of the flow space is substantially at the end of inlet pipe 12. Conical gas flow director 69 may have a constant diameter part over a certain length at its end. In this embodiment, the width of the flow space remains constant over said length in the axial direction, after narrowing down before that. This provides for a more regular flow of the first gas stream beyond the end of inlet pipe 12.

[0071] In the illustrated embodiment, the end of conical gas flow director 69 lies substantially at the same axial position as the end of inlet pipe 12, or upstream. That is, conical gas flow director 69 does not extend axially beyond the end of inlet pipe 12. Fouling of conical gas flow director 69 due to the plasma is prevented because conical gas flow director 69 does not extend beyond the end of inlet pipe 12. In another embodiment, conical gas flow director 69 may extend axially beyond the end of inlet pipe 12, conical gas flow director 69 having a diameter that decreases beyond the end of inlet pipe 12 to prevent fouling.

[0072] Solvent is circulated or refreshed for control of the temperature and solute concentration, using solvent inlet 62a and outlet 62b. Solvent may be provided in a volume with a maximum height defined by outlet 62 for example. A Collison nebulizer is used that radially injects droplets into an axially directed gas stream in inlet pipe. Collison gas is fed though inlet 63. An additional gas flow 61 is supplied, that is tangentially injected to transport liquid aerosols to the plasma activated volume.

[0073] Although fluid bed based solid particle supply and nebulizer based liquid particle supply have been shown in specific device configurations by way of example, it should be appreciated that they may be used in any configuration. Other types of powder particle supply may be used. A tray with a radially extending surface may be provided in inlet pipe, a gas stream blowing through the tray to carry powder particles from the tray during operation.

[0074] The gas streams may be generated by applying pressure differences between the inlets and outlets, for example using one or more pumps (not shown). Filters may be provided at the inlet and/or outlets.

[0075] Figure 7 shows an embodiment with a particle source 70 (a nebulizer for supplying liquid particles or a solid particle source), a gas supply chamber 74, with an inlet 77 and a surplus liquid outlet 76, a substrate 80 and a transport system 78. Gas supply chamber 74 is coupled to the input of inlet pipe 12. Particle source 70 and inlet 77 are coupled to gas supply chamber. Substrate is located at an output of dielectric reactor pipe 14, transverse to the axial direction of dielectric reactor pipe 14. Transport system 78 is configured to transport substrate 80 transverse to the axial direction of dielectric reactor pipe 14. Transport system 78 may comprise a pair of rollers.

[0076] In operation particles and gas are mixed in gas supply chamber 74 and the first gas stream of mixed particles and gas is supplied from gas supply chamber 74 through inlet pipe to the reactor. From the reactor particles are fed to substrate 80, where they are collected. This embodiment may be used to deposit plasma-activated liquid particles, eventually comprising solid particles, to form a coating layer, for example a polymer coating, on substrate 80 while preventing the formation of a coating layer on dielectric reactor pipe 14.

[0077] Surface modification and coating of powder materials can be used for:

- Improved dispersion: Powders with high surface to volume ratio are often difficult to disperse in liquid material (for example during production of polymer based composites) because of strong agglomeration, electrostatic behavior, hygroscopic behavior, or poor wettability. Modification (generally increase) of the surface energy is often required.
- Adhesion improvement: The structural properties of composite materials, such as tensile strength and toughness under impact dynamic conditions, are dependent on added micron or nano-sized filler materials during manufacturing. The structural properties can be dramatically improved by their adhesion improvement of the filler material.
- Cleaning, disinfection or sterilization
- Prior to coating or further processing plasma powder processing can be used for removal of undesirable material which is attached on powder particles. Plasma powder processing can be used to inactivate microorganisms in a gas stream or microorganisms attached to powder particles.
- Isolation of the powder material from its environment: Coating of powders is often desired to improve aging properties. For instance coatings on metal powders can be used to avoid oxidative corrosion (passivation). TiO_2 particles used in large quantities as UV blocking filler in plastics can be coated to avoid undesirable chemical reaction with the polymer matrix. In case of food and medical applications coatings on powders can solve problems of biological or chemical incompatibility. Encapsulation of micron sized particles (microencapsulation) is already used to control function, taste, odor and aging properties of food and (nanosized) pharmaceutical products. Coatings are thus used to immobilize and protect ingredients from undesirable physical diffusion or chemical reaction.
- Controlled release: Coatings on powder materials are used for example for delayed or programmed drug release in the human body.
- Controlled reactivity: In the domain of energetic materials (explosives, munitions, pyrotechnical materials), coating of powder materials can be beneficially applied to tailor desired properties to specific needs. For instance, ignition temperatures and burning rates of metal particles can be controlled providing inert or reactive thin coatings. Even multilayer coatings can be of interest in order to shorten or delay ignition rates in combination with enhanced burning rates. Coating of powder ingredients of energetic compositions can be very beneficial to obtain formulations or composites of otherwise physically or chemically incompatible materials.

[0078] The deposition of nanometer thin coatings on micron sized powder, possibly trapping nanoparticles within those thin layers on micron sized particles, is a promising tool to stabilize energetic nanomaterials. Such approach may solve the existing problems associated with production, storage and dispersion of isolated nanosized powders in energetic compositions. Further energetic material applications include thin coatings of powders for reduced sensitivity towards shock initiation and frictional or electrostatic ignition.

[0079] A summary list of energetic material applications include: increased reaction rates by coating an oxidizer on a fuel, for instance Silicon-Fluorine containing coatings on Aluminum powder (including submicron A1 material), composing structural materials with or without loosing energetic capabilities, e.g. ignition sensitivity, viz. A1 or Mg coatings on $KC1O_4$. KNO_3, $KMnO_4$ or $Sr(NO_3)_2$ powders, controlling the reactivity of Metastable Intermolecular Composites (MICs), e.g. Fe_2O_3 coating on $KMnO_4$ powder, avoiding compatibility problems with ingredients in explosives, propellants and gas generators, and protecting from moisture, humidity.

[0080] The invention is not restricted to the embodiments described herein.

[0081] Further such variants will be apparent to the person skilled in the art and are considered to lie within the scope of the invention as defined in the following claims.

Claims

1. A plasma powder processing apparatus for processing powder particles in a reactor chamber, the ap-

paratus comprising

- a dielectric pipe, forming a surrounding wall of the reaction chamber along at least part of a length of an axis of the reaction chamber, the dielectric pipe extending beyond a transverse boundary of the reaction chamber at an inlet end of said length;
- a particle material stream inlet pipe extending coaxially with said dielectric pipe within said dielectric pipe, a downstream end of the particle material stream inlet pipe defining the axial position of the transverse boundary;
- a first and second electrode structures facing each other from an outer and inner radial position respectively, with at least part of a radial extent of the dielectric pipe between first and second electrode structures, the second electrode structure comprising mutually spaced conductor lines, separated by non-conducting spaces, the second electrode structure defining a surface dielectric barrier discharge plasma region, covering a majority of the circumference of the dielectric pipe, at least on a part of the dielectric pipe upstream of the downstream end of the particle material stream inlet pipe;
- plasma carrier gas inlet coupled to a space between the dielectric pipe and the particle material stream inlet pipe and configured to provide a plasma carrier gas stream between the dielectric pipe and the particle material stream inlet pipe towards the reactor chamber.

2. A plasma powder processing apparatus according to claim 1, wherein the mutually spaced conductor lines are provided on the inner surface of the dielectric pipe.

3. A plasma powder processing apparatus according to claim 1 or 2, wherein the mutually spaced conductor lines extend downstream beyond the downstream end of the particle material inlet pipe, the surface dielectric barrier discharge plasma region covering a part of the dielectric pipe downstream of the downstream end of the particle material stream inlet pipe.

4. A plasma powder processing apparatus according to any one of the preceding claims, comprising a voltage generator with outputs electrically coupled to the first and second electrode structure, the voltage generator being configured to apply a voltage with a non zero DC component and an AC component between the first and second electrode structure.

5. A plasma powder processing apparatus according to any one of the preceding claims, comprising an electrical discharge electrode structure located within the inlet pipe upstream of the downstream end of inlet pipe.

6. A plasma powder processing apparatus according to any one of the preceding claims, comprising a flow shaper, having a conical shape extending from within the inlet pipe to beyond the downstream end of the inlet pipe and narrowing down downstream in the axial direction.

7. A plasma powder processing apparatus according to claim 6, comprising a vibrator, wherein the flow shaper is mounted on the vibrator.

8. A plasma powder processing apparatus according to any one of the preceding claims, comprising a conical gas flow director within the inlet pipe, widening downstream in the axial direction along at least part of its length.

9. A plasma powder processing apparatus according to claim 8, comprising a constant width passage between the conical gas flow director and the inlet pipe, from an end of a widening portion of the conical gas flow director until the downstream end of the inlet pipe.

10. A plasma powder processing apparatus according to any one of the preceding claims wherein a distance between an outer surface of the inlet pipe and the inner surface of the dielectric pipe lies in a range from 0.2 to 2 millimetres.

11. A plasma powder processing apparatus according to any one of the preceding claims wherein the second electrode structure comprises conductor lines with a width in a range of 0.5 to 2 millimetres with non-conductive spaces having a width in a range of 2 to 10 millimetre between the conductor lines.

12. An apparatus according to any one of the preceding claims, wherein the dielectric pipe and the particle material stream inlet pipe have circular radial cross-sections.

13. An apparatus according to any one of the preceding claims, wherein the dielectric pipe and the particle material stream inlet pipe have elongated rectangular cross-sections with a length width ratio of at least five to one.

14. A method of plasma processing of powder particles, the method comprising the steps of:

- supplying a first gas stream, containing particle material to be processed, from an inlet pipe into a dielectric pipe that extends coaxially with the

inlet pipe surrounding the inlet pipe and beyond a downstream end of the inlet pipe;
- supplying a second gas stream comprising a plasma carrier gas into a space between the inlet pipe and the dielectric pipe and from there into the dielectric pipe beyond a downstream end of the inlet pipe;
- generating a surface dielectric barrier plasma discharge along the inner surface of the dielectric pipe using spaced conductor lines defining a surface dielectric barrier discharge plasma region covering an inner surface of the dielectric pipe along a majority of the inner circumference of the dielectric pipe at least on a part of the dielectric pipe upstream of the downstream end of the particle material stream inlet pipe.

15. A method according to claim 14, comprising imparting net charge to the first and second gas stream, of mutually equal or opposite polarity.

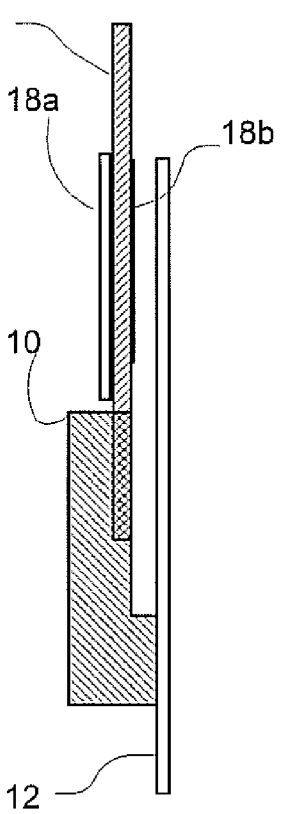

Fig.1a

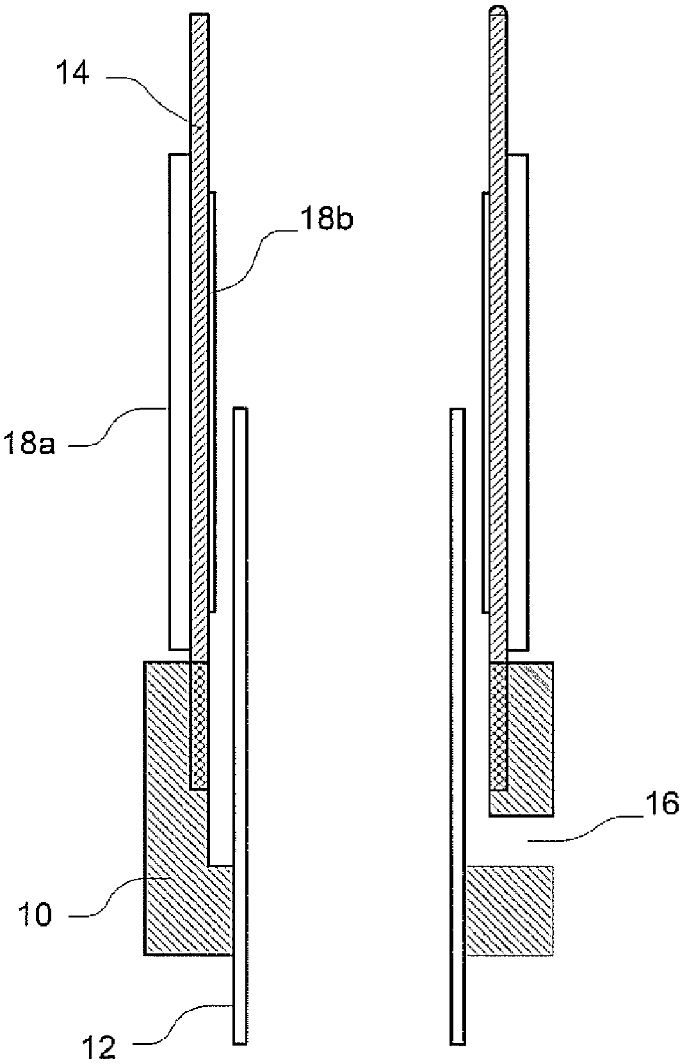

Fig. 1

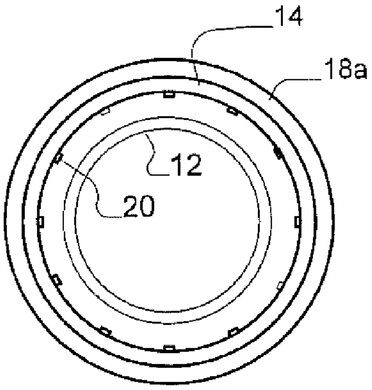

Fig. 2a

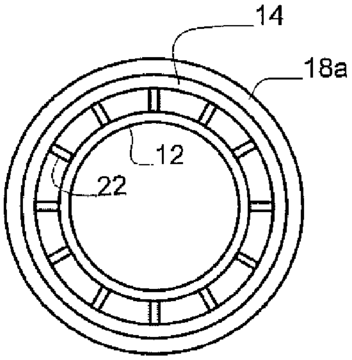

Fig. 2b

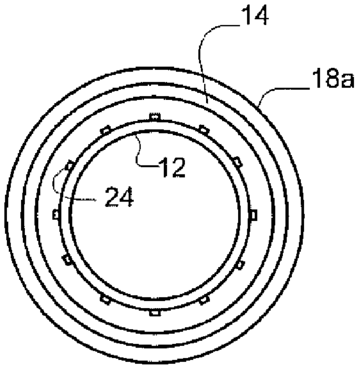

Fig. 2c

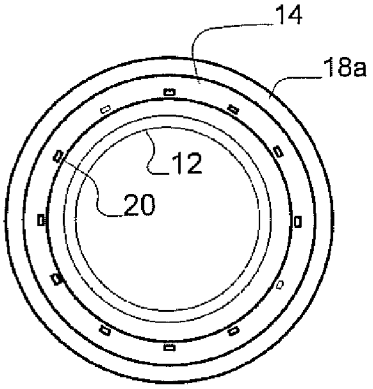

Fig. 2d

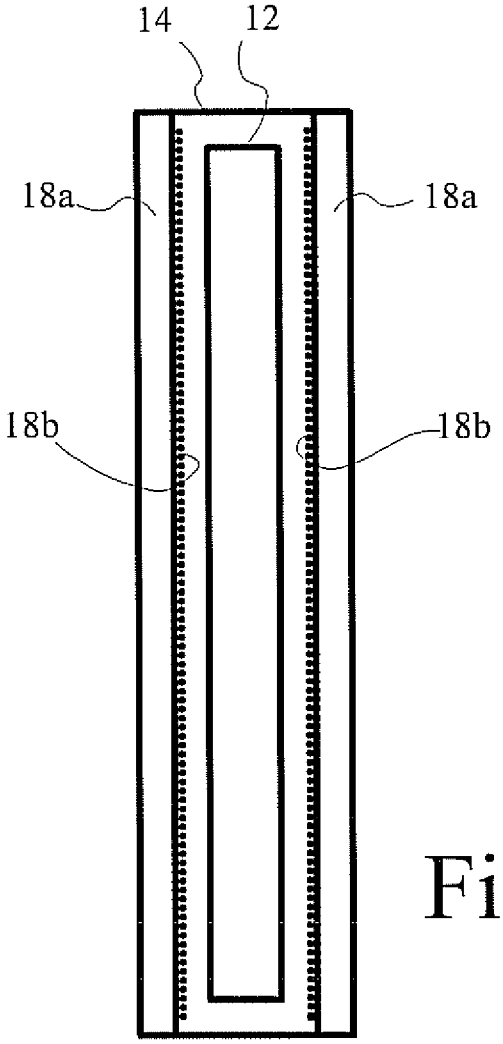

Fig.2e

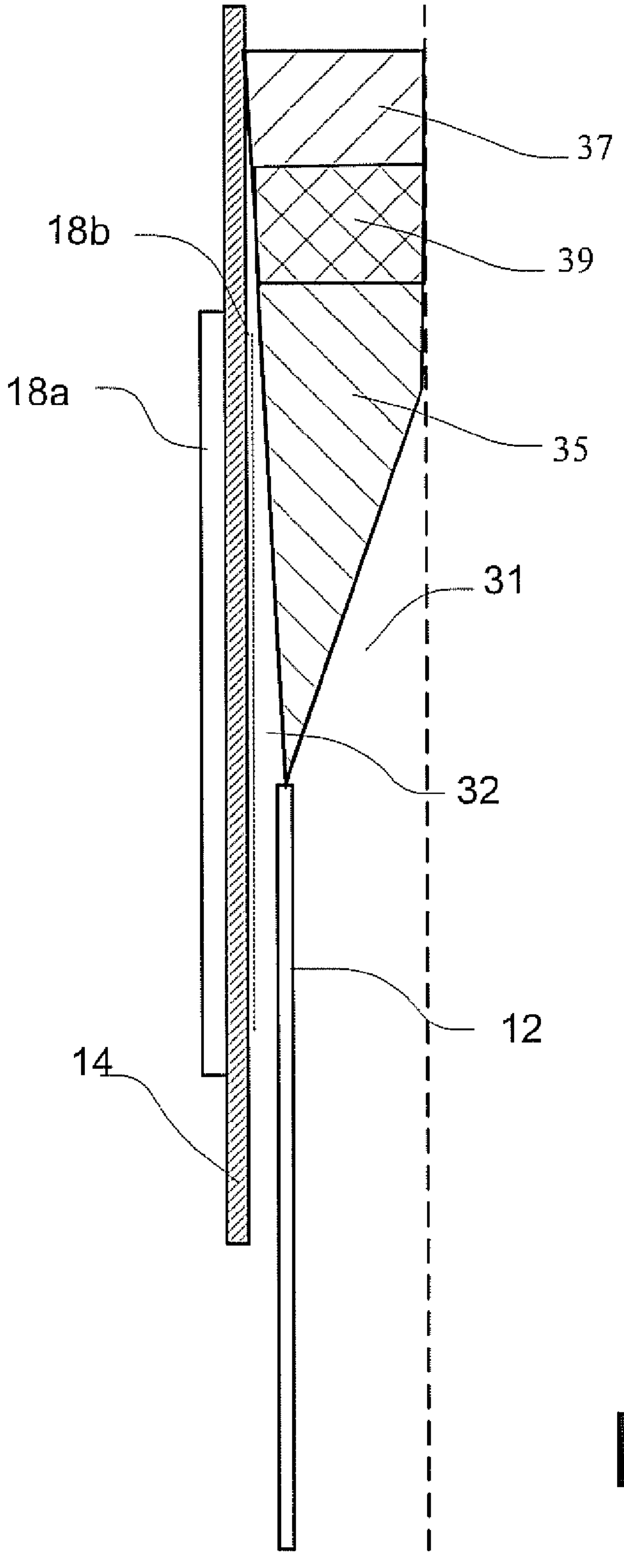

Fig. 3

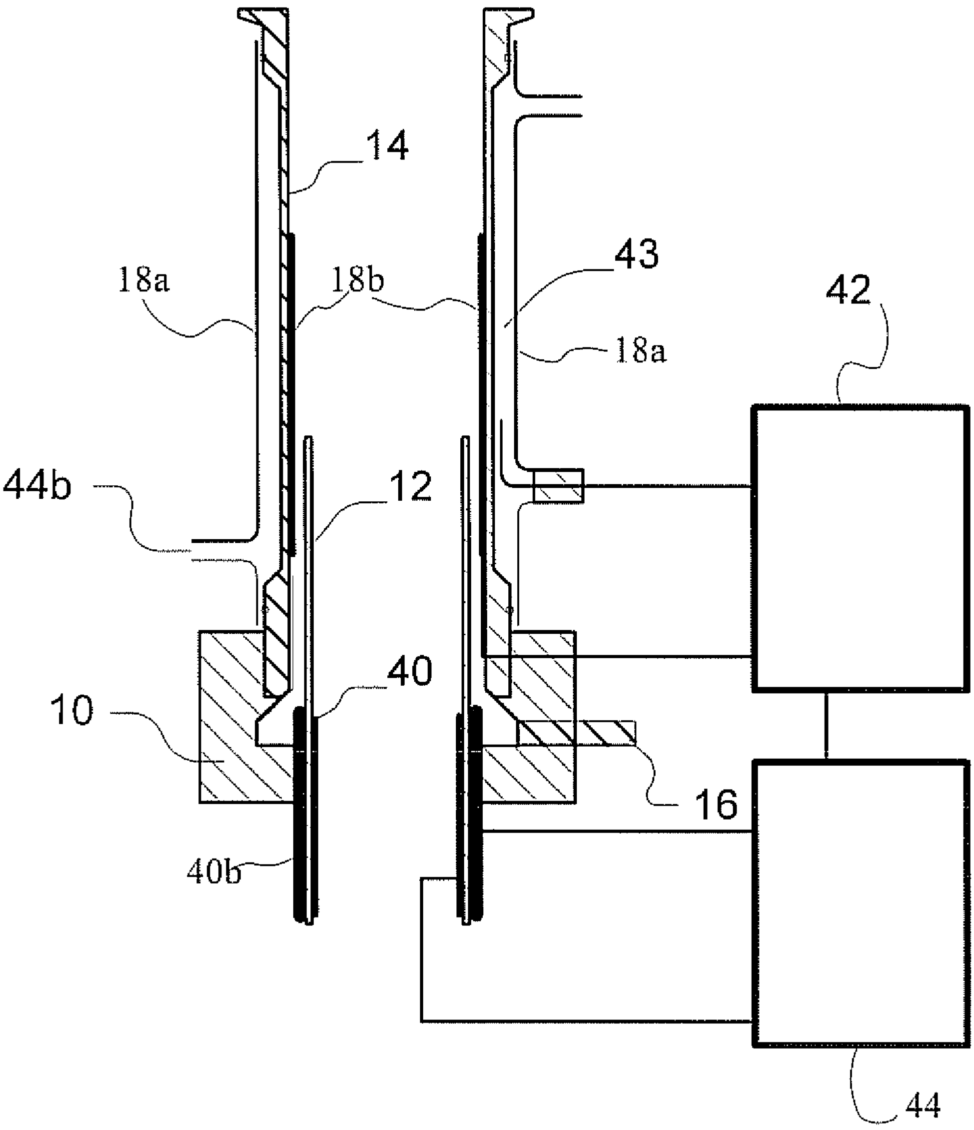

Fig. 4

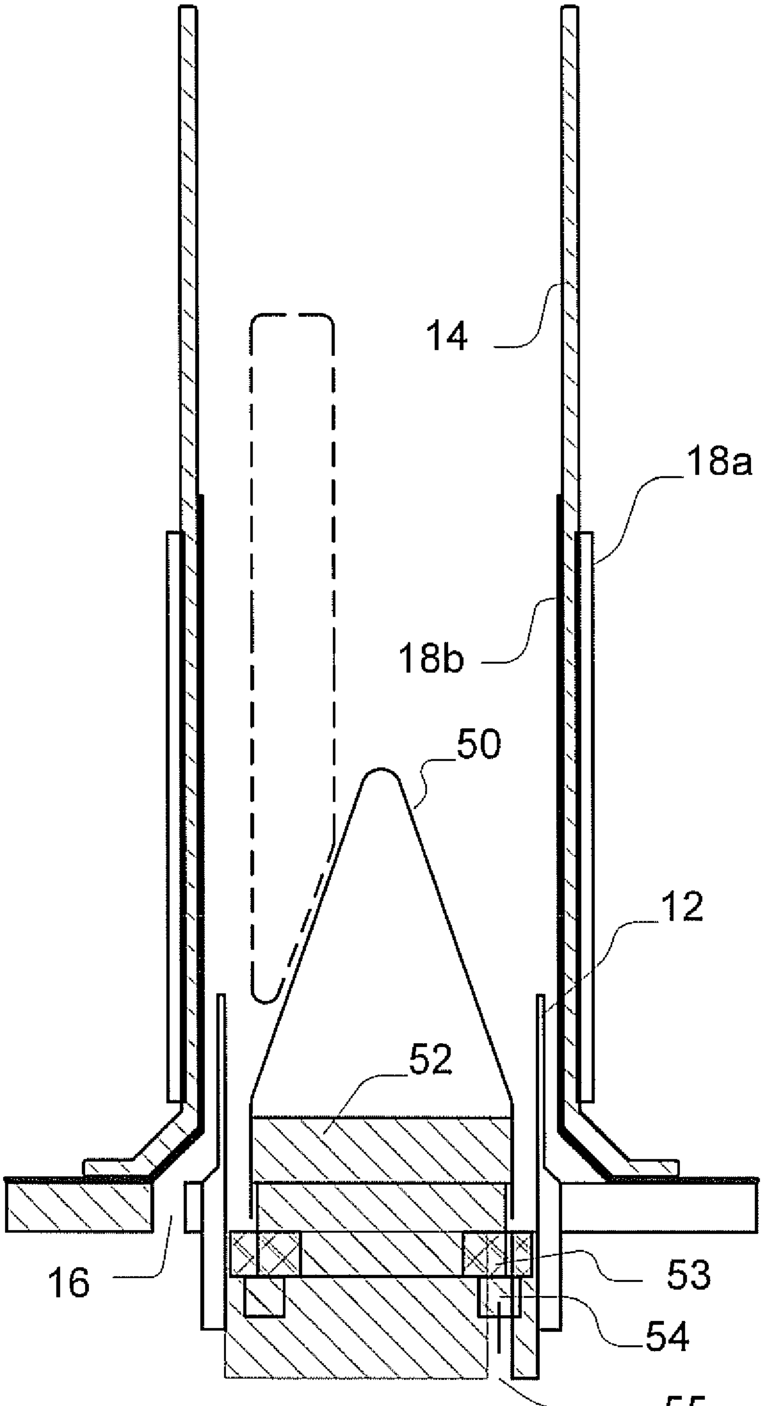

Fig. 5

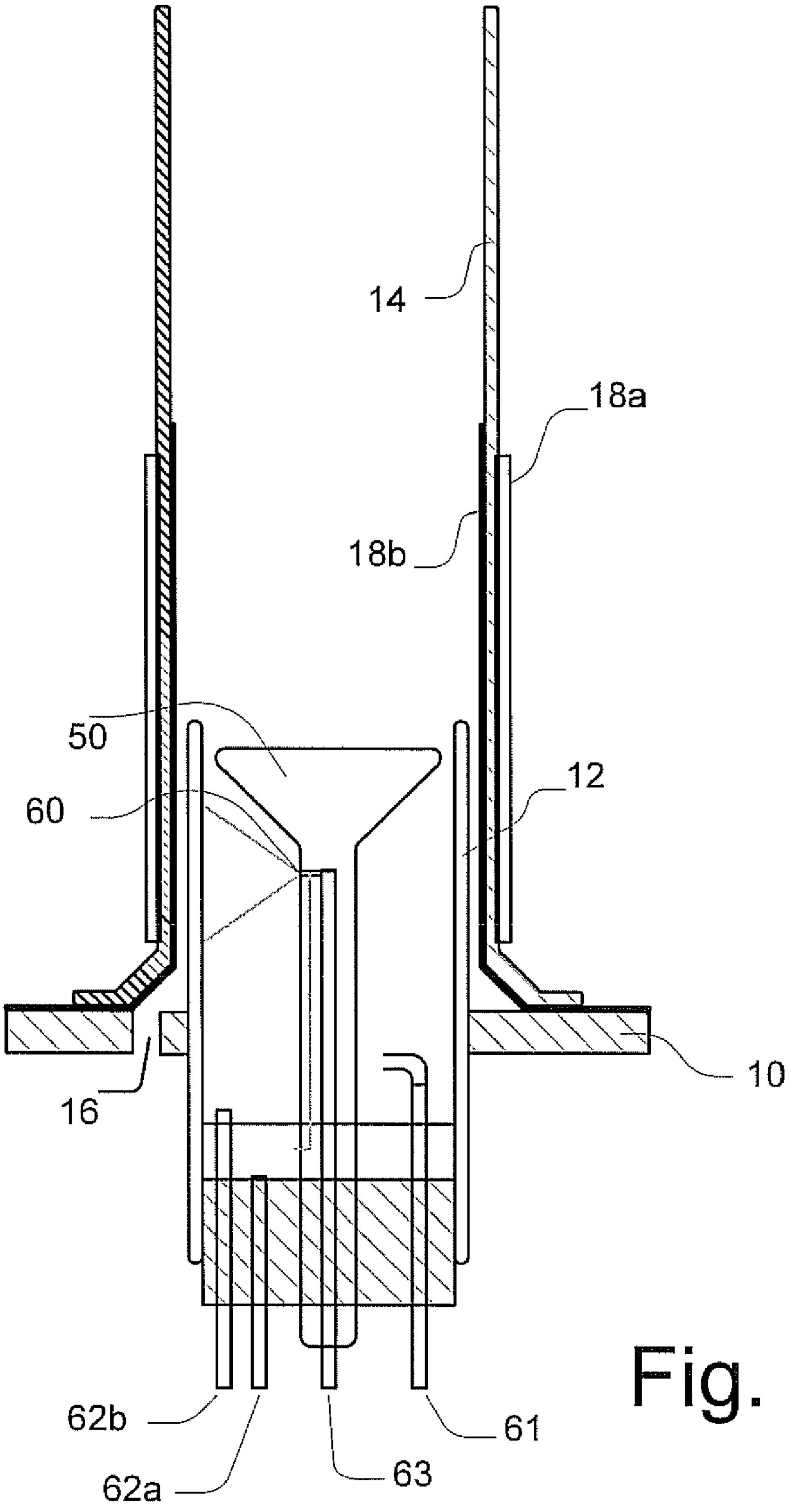

Fig. 6

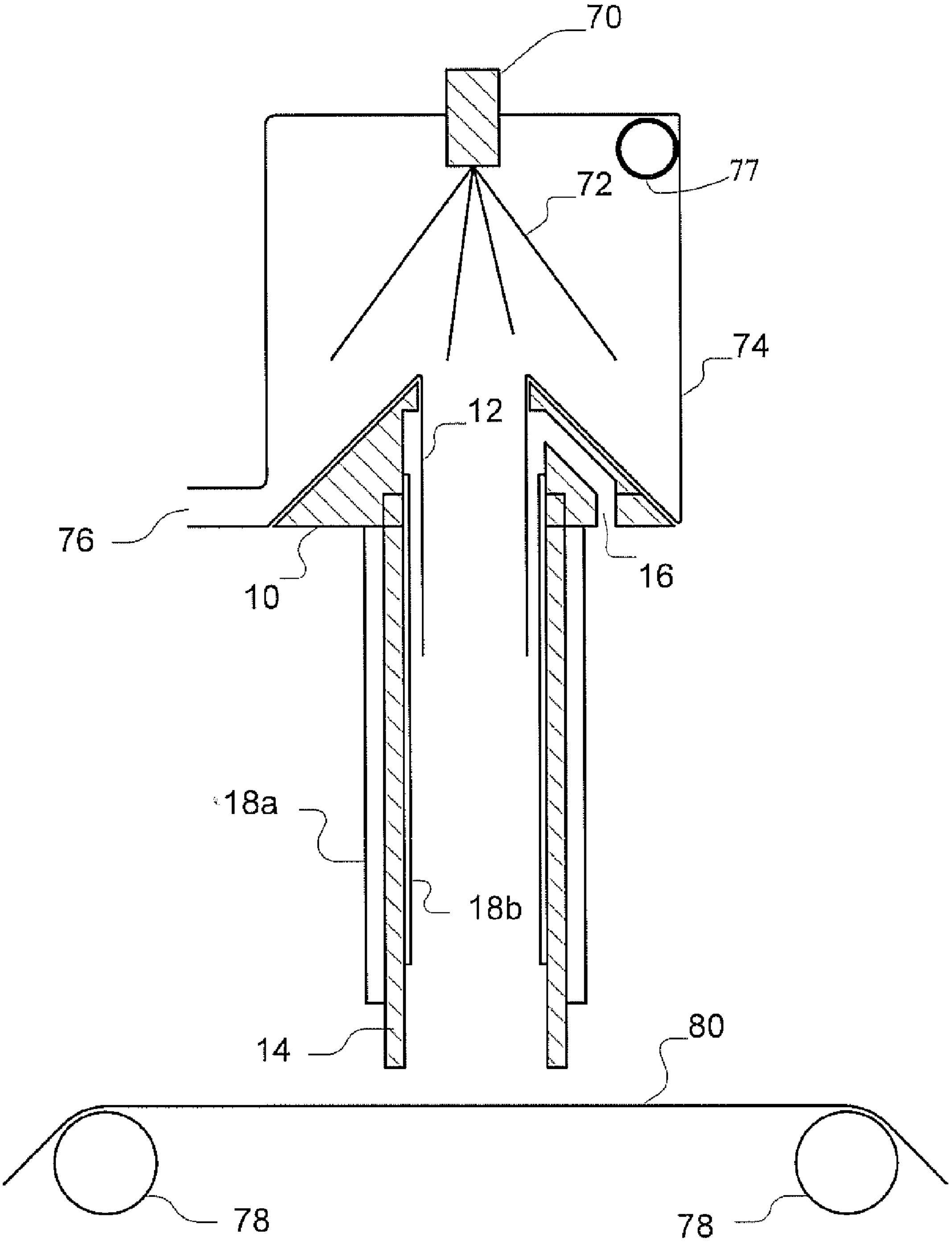

Fig. 7

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EUROPEAN SEARCH REPORT

Application Number
EP 10 17 4177

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2004/037756 A1 (HOUSTON EDWARD J [US] ET AL HOUSTON JR EDWARD J [US] ET AL) 26 February 2004 (2004-02-26) * abstract; figures 1a-d,f * * paragraphs [0004], [0008], [0010], [0040], [0041], [0046] - [0050] * -----	1,3,4,6, 8,10-15	INV. H05H1/24
X	WO 2007/067924 A2 (STRYKER CORP [US]; HOUSTON EDWARD J [US]) 14 June 2007 (2007-06-14) * abstract; figure 3 * -----	1,2,14	
A	US 2005/236374 A1 (BLANKENSHIP GEORGE D [US]) 27 October 2005 (2005-10-27) * abstract; figure 8 * -----	1-15	
			TECHNICAL FIELDS SEARCHED (IPC)
			H05H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	2 February 2011	Crescenti, Massimo

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 10 17 4177

02-02-2011

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US 2004037756 A1	26-02-2004	NONE	
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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- **TAKAFUMI NAKAJIMA et al.** Development of powder antifoamer by atmospheric pressure glow plasma. *Thin Solid Films,* 2001, vol. 386, 208-212 **[0007]**