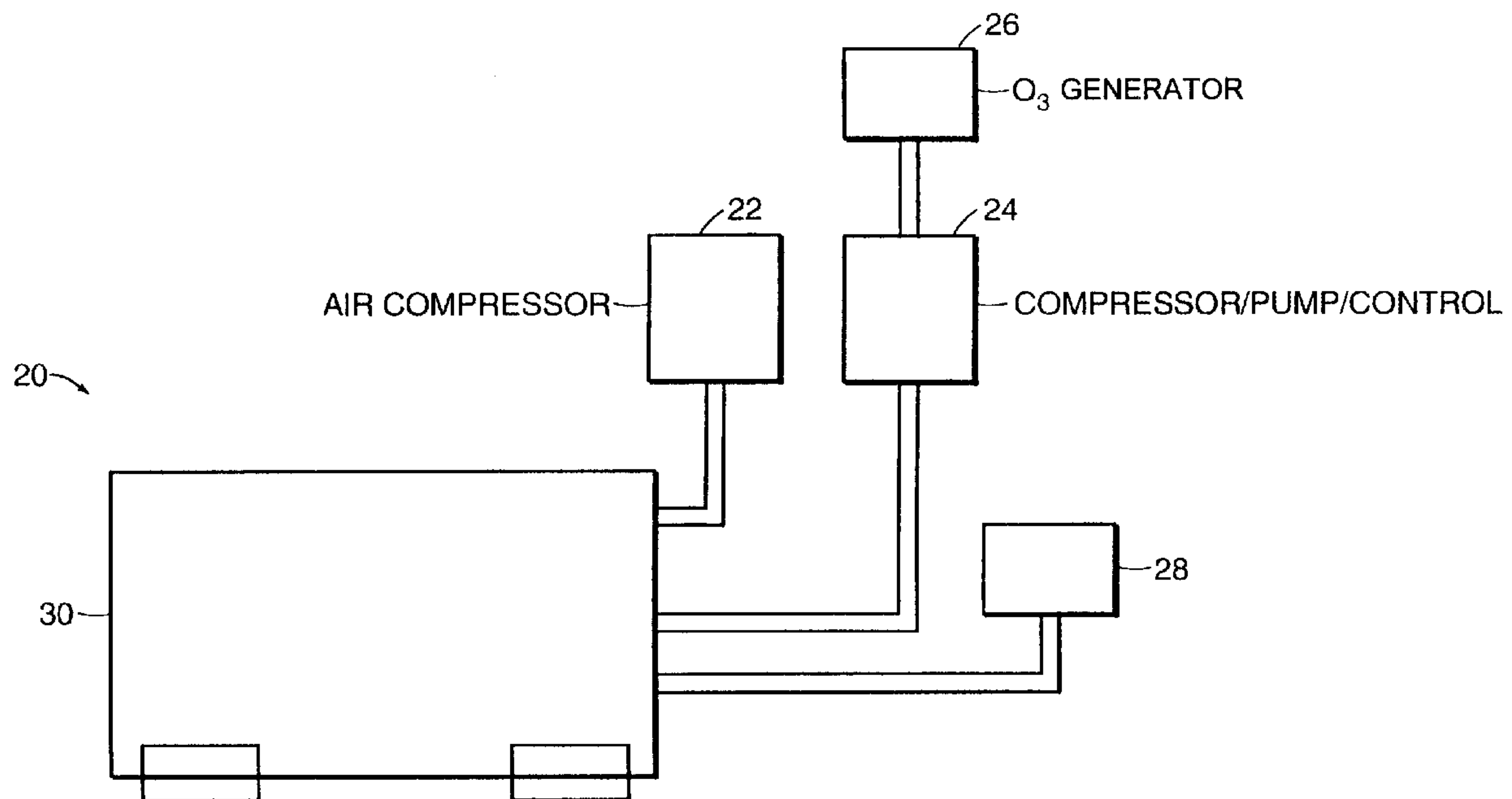




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(54) Titre : BOITIER DE CAPTAGE DE SOURCE POUR DECONTAMINATION DE L'EAU  
 (54) Title: SPRINGBOX FOR WATER REMEDIATION



(57) Abrégé/Abstract:

A method and apparatus for treatment of contaminated water is described. The apparatus includes a container divided into at least two chambers by a wall that partially separates the two chambers, the containing having an inlet at a first one of the chambers and an outlet at a second one of the chambers. The apparatus has a first microporous diffuser disposed in a first one of the chambers of the container and arranged to receive a decontaminating gaseous agent and a second microporous diffuser disposed in a second one of the chambers and arranged to receive air. Additionally, special microporous diffusers are described.

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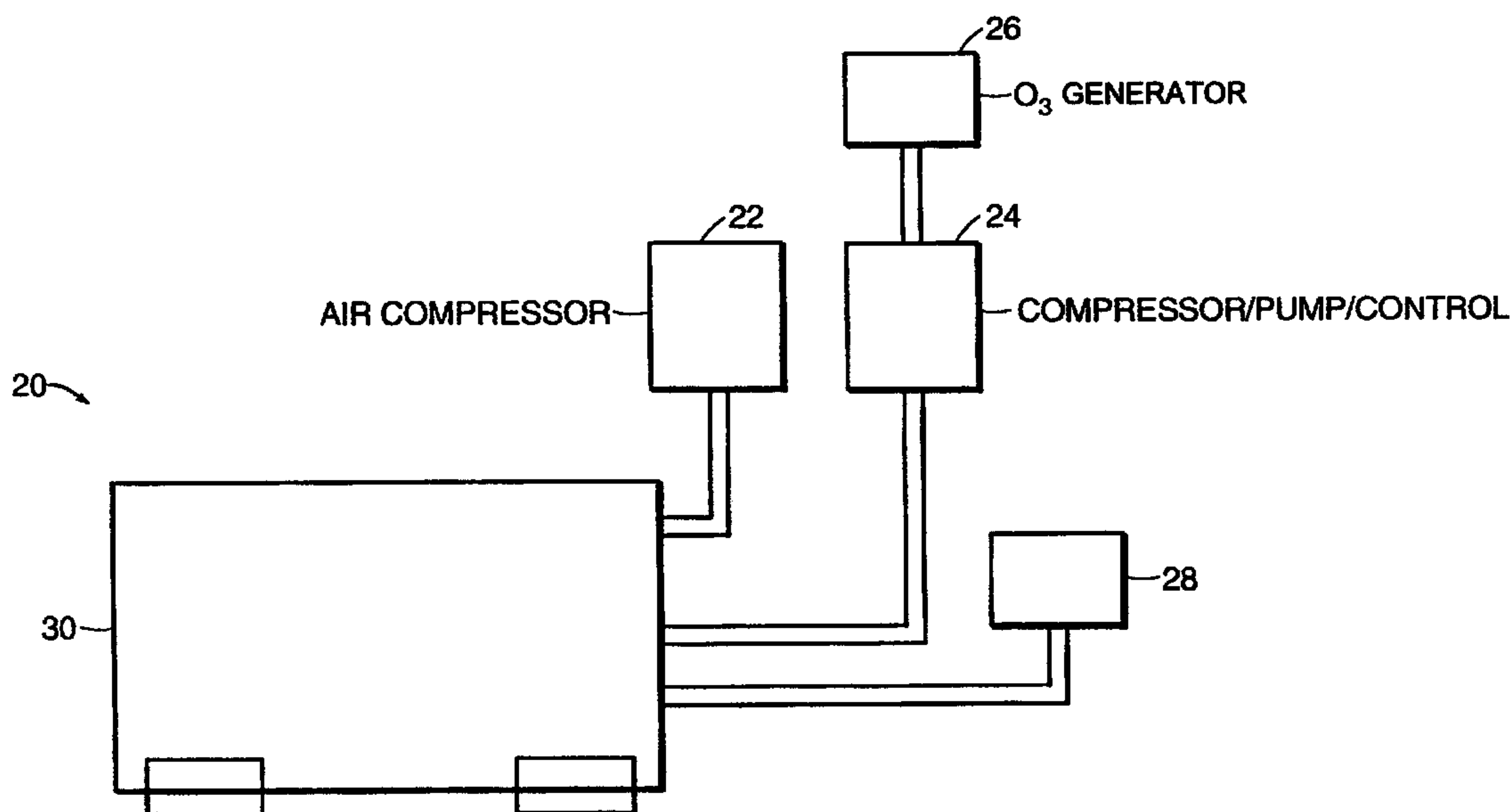
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(54) Title: SPRINGBOX FOR WATER REMEDIATION



(57) Abstract: A method and apparatus for treatment of contaminated water is described. The apparatus includes a container divided into at least two chambers by a wall that partially separates the two chambers, the containing having an inlet at a first one of the chambers and an outlet at a second one of the chambers. The apparatus has a first microporous diffuser disposed in a first one of the chambers of the container and arranged to receive a decontaminating gaseous agent and a second microporous diffuser disposed in a second one of the chambers and arranged to receive air. Additionally, special microporous diffusers are described.

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## SPRINGBOX FOR WATER REMEDIATION

## BACKGROUND

This invention relates generally to water remediation systems.

5           There is a well recognized need to clean-up  
contaminants that exist in ground and surface water. In  
particular, there is one type of contamination problem  
which widely exists, that is, the contamination of  
surface waters or subsurface waters which find their way  
10 to the surface such as, for example, in a contaminated  
spring. Such surface waters may be contaminated with  
various constituents including volatile hydrocarbons,  
such as chlorinated hydrocarbons including  
trichloroethene (TCE), tetrachloroethene (PCE).

15

## SUMMARY

According to an aspect of the present  
invention, an apparatus for treatment of contaminated  
water includes a container divided into at least two  
20 chambers by a wall that partially separates the two  
chambers, the containing having an inlet at a first one  
of the chambers and an outlet at a second one of the  
chambers. The apparatus also includes a first  
microporous diffuser disposed in a first one of the  
25 chambers of the container and arranged to receive a  
decontaminating gaseous agent and a second microporous  
diffuser disposed in a second one of the chambers and  
arranged to receive air.

According to an aspect of the present  
30 invention, a spring box apparatus for treatment of  
contaminated groundwater includes a container divided  
into a plurality of partially closed chambers by a

plurality of walls each of which partially separates adjacent chambers and a plurality of microporous diffusers arranged in the corresponding plurality of chambers, with a first portion of the microporous  
5 diffusers coupled to a gaseous decontamination agent source, and a remaining portion of the microporous diffuser being coupled to an air source.

According to an aspect of the present invention, an method of treating groundwater received  
10 from a spring includes introducing the groundwater into a spring box having at least one microporous diffuser disposed therein, said microporous diffuser delivering microfine bubbles containing air/ozone to the water introduced into the box.

15

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagrammatical view of a typical surface water treatment example.

FIG. 2 is a block diagram of an apparatus used  
20 in the treatment process.

FIGS. 3A and 3B are respectively plan and elevational views somewhat schematic, of a spring box used in the apparatus of FIG. 2.

FIGS. 3C and 3D are plan and elevational views  
25 of still alternate spring box arrangements.

FIGS. 4A and 4B are longitudinal cross-section and plan cross-sectional views of a microporous diffuser useful in the spring box of FIGS. 3A and 3B;

FIGS. 5A, 5B are longitudinal cross-section and  
30 plan cross-sectional views, respectively, of an alternative microporous diffuser useful in the spring box of FIGS. 3A and 3B.

FIGS. 6A and 6B are cross-sectional view of sidewalls of the microporous diffusers of either FIGS. 4A, 4B or 5A, 5B showing exemplary construction details.

FIGS. 7A, 7B are longitudinal cross-section and  
5 plan cross-sectional views, respectively, of a still alternative microporous diffuser useful in the spring box of FIGS. 3A-3D.

FIGS. 8A and 8B are respectively plan and elevational views somewhat schematic, of a circular  
10 spring box arrangement with a mixing feature also useful in the apparatus of FIG. 2.

FIG. 9 is a cross-sectional view showing an alternative treatment example.

FIG. 10 is a plot of removal rate of PCE for an  
15 aqueous solution equivalent to 120 ppb, over differing bubble sizes.

#### DETAILED DESCRIPTION

Referring now to FIG. 1, an example 10 of the  
20 use of an apparatus for treatment of surface water or in-situ removal of contaminants from water is shown. Illustrated in FIG. 1 is a site 11, having a subsurface aquifer 14 that produces surface waters 12 such as by a spring. A spring-box treatment system 20 disposed on the  
25 site 11. The spring box treatment system 20 is disposed to intercept the surface water 12 and to divert the surface water into the spring box treatment system 20 to remove contaminants such as volatile hydrocarbons and, in particular, chlorinated hydrocarbons which may exist in  
30 the water in the aquifer 14. The spring box treatment system 20 outputs a water stream 16 which is substantially free of the contaminants.

Contaminants which can be treated or removed by use of the spring box treatment system 20 include hydrocarbons and, in particular, volatile chlorinated hydrocarbons such as tetrachloroethene, trichloroethene, 5 cisdichloroethene, transdichloroethene, 1-1-dichloroethene and vinyl chloride. In particular, other materials can also be removed from the stream including chloroalkanes, including 1,1,1 trichloroethane, 1,1, dichloroethane, methylene chloride, and chloroform; 10 benzene, toluene, ethylbenzene, O-xylene, P-xylene, naphthalene and methyltetra-butylether (MTBE). It should be understood that the use of the spring-box treatment system 20 is not limited to flowing surface water but could be used to treat pumped or stored water.

15 Referring now to FIG. 2, the spring box treatment system 20 includes a spring box 30, and an air compressor 22, a compressor/pump control mechanism 24, and an ozone (O<sub>3</sub>) generator 26. The air compressor 24 can feed a stream of air into the spring box 30 whereas, the 20 compressor pump control 24 feeds a stream of air mixed with ozone (O<sub>3</sub>) from the ozone generator 26 into the spring box 30 to affect substantial removal of the above-mentioned or similar types of contaminants. Optionally, or in addition thereto, the apparatus 20 can also include 25 a pump 28 that supplies a liquid decontamination agent such as hydrogen peroxide or such as catalyst agents including iron containing compounds such as iron silicates or palladium or palladized carbon. To promote biodegradation reactions, the liquid introduced can be a 30 nutrient mixture of nitrogen (ammonium or nitrate), phosphorus, and potassium along with oxygen as a gas to

promote oxidic reactions or carbon dioxide and hydrogen sulfide to promote reduction reactions.

The spring box 30 uses primarily a gas-gas reaction between contaminant vapors and ozone (described below). This reaction can be supplemented with a liquid phase reaction. A liquid decontaminator such as hydrogen peroxide can also be used. The use of hydrogen peroxide as a thin film coating on the bubbles promotes the decomposition rate by adding a secondary liquid phase reactive interface as volatile compounds enter the gaseous phase. It also expands the types of compounds that can be effectively removed. Alternatively, the pump control 28 can simply feed water.

Referring now to FIGS. 3A and 3B, an arrangement of a spring box 30 is shown. The spring box includes a container 31 comprised of a sidewall 32 of a durable material such as concrete over which is disposed or attached a water tight lid 33 also comprised of concrete. Within the spring box 30 is provided an inlet port 42 to receive the water from the spring, as well as a plurality of partially closed chambers 40a-40d which are formed within the interior of the spring box by walls or partitions 38a-38c. Within each of the chambers 40a-40d are disposed a plurality of microporous diffusers such as those shown in conjunction with my issued U.S. Patent No. 5,855,775 which is incorporated herein by reference. Alternatively, microporous diffusers 50, 70, as described below in conjunction with FIGS. 4A and 4B or FIGS. 5A and 5B may be used.

In the arrangement shown in FIG. 3A, a first pair of microporous diffusers 50a, 50b or 70a, 70b are coupled to a common gas/liquid feed arrangement 36a which

can be fed, for example, from compressor/pump 24 and compressor 28 (FIG. 2). The spring box 30 also includes a second feed arrangement 38b which in this embodiment has one of the microporous diffusers 50c, 70c being fed with a combination of air, ozone and air, ozone and liquid as above, and with the second microporous diffuser 50d, 70d being fed only by air to provide air stripping of any residual ozone before exiting of the treated water.

10 As shown in FIG. 3B, the microporous diffusers are arranged in elevation above the bottom of the spring box 30 within a pool 39 of water provided from the spring or other surface water source.

15 FIGS. 3C and 3D show still alternate spring box arrangements. In the arrangement 30' of FIG. 3C, the diffusers 50 or 70 are coupled in series whereas FIG. 3D shows diffusers 50, 70 arranged to be staggered in elevation over the height of the spring box.

20 The spring box 30 is an ozone reactor vessel in which ozone is pumped into the pool of water through the use of the microporous diffusers. The microporous diffusers are disposed in the water under treatment and transfer ozone into the water in the form of microfine or fine bubbles which promote rapid gas/gas/water reactions with volatile organic compounds particularly in the presence of a catalyst or enhancer which may participate in the gaseous phase of the reaction, instead of solely enhancing dissolved aqueous disassociation and reactions. In addition, with the optional use of the liquid port to the apparatus, the gas/gas reactions are optimized to include gas/gas reactions within the gaseous phase as well as inducing water aqueous phased reactions to

25  
30

achieve an overall decomposition rate within the gaseous phase and the aqueous phase from second water reactions. For example, the use of hydrogen peroxide as a laminate coating on the bubbles can enhance decomposition rates as mentioned below. The micron plastic bubblers may also be coated with or have sintered into construction an outer layer of activated carbon or activated carbon with palladium to simultaneously accumulate and promote decomposition of the chloroethenes.

The production of microbubbles and selection of appropriate size distribution are selected for optimized gas exchange through high surface area to volume ratio and long residence time within the liquid to be treated. The microbubbles are generated by using microporous materials in the microporous diffuser 50 that acts as a bubble chamber, as shown in the embodiment 50 (FIG. 4A-4B) or, alternatively, through the embodiment 70 of the microporous diffuser of FIG. 5A-5B. The apparatus 20 promotes the continuous production of microbubbles minimizing coalescing or adhesion. The injected air/liquid combination moves as a fluid into the water to be treated; whereas, microencapsulated ozone within the microfine bubbles enhances and promoted in-situ stripping of volatile organics and simultaneously terminates normal reversible Henry's reaction.

Referring now to FIGS. 4A-4B, a microporous diffuser 50 is shown. The microporous diffuser 50 includes a first cylindrical member 56 comprised of a hydrophobic material which provides an outer cylindrical shell for the microporous diffuser 50. The cylindrical member 56 has a sidewall 56a which is comprised of a large plurality of micropores. A second cylindrical

member 60 is coaxially disposed within the first cylindrical member 56. The second cylindrical member 60 is comprised of a hydrophobic material and has a sidewall 60a which is comprised of a large plurality of micropores. Also disposed within the confines of the first cylindrical member 56 are a plurality of cylindrical members 58, here four, which have sidewalls 58a having a large plurality of micropores and also comprised of a hydrophobic material.

A proximate end of central cylindrical member 60 is coupled to a first inlet port 52a which is provided from a first inlet cap 52 and proximate ends of the plurality of cylindrical members 58 are coupled to second inlet ports generally denoted as 52b. At the opposite end of the microporous diffuser 50 an end cap 54 covers distal ends of cylindrical members 56 and 60. Here distal ends of the plurality of cylindrical members 58 are sealed by separate caps 59 but could be terminated by the end cap 54. The end cap 54 in conjunction with cap 52 seals the distal ends of the microporous diffuser. Each of the cylindrical members 56, 58 and 60 are here cylindrical in shape and have a plurality of microscopic openings constructed through sidewalls 56a, 58a and 60a, respectively, thereof having pore sizes matched to or to create a pore size effective for inducing gas/gas reactions in the spring box 30. Sidewalls of each of the cylindrical members can have a pore diameter in a range of 1-200 microns, preferably 1-50 microns and more preferably 5-20 microns. The combination of the inlet cap 52 and end cap 54 seals the microporous diffuser 50 permitting liquid and gas to escape by the porous construction of sidewalls of the microporous diffusers.

The microporous diffuser 50 can be filled with a microporous material such as microbeads with mesh sizes from 20 to 200 mesh or sand pack or porous hydrophilic plastic to allow introducing a liquid into the pore spaces where liquid is exiting.

Referring now to FIGS. 5A and 5B, an alternate embodiment 70 of a microporous diffuser is shown. The microporous diffuser 70 includes an outer cylindrical member 76 having a sidewall 76a within which is disposed an inner cylindrical member 78 having a sidewall 78a. The inner cylindrical member 78 is spaced from the sidewall of the outer cylindrical member. The space 77 between the inner and outer cylindrical members 76, 78 is filled with a packing material comprised of glass beads or silica particles (silicon dioxide) or porous plastic which, in general, are hydrophilic in nature. This space is coupled to an input port 72b which receives liquid, and catalysts, and/or nutrients from pump 39 (FIG. 2). The microporous diffuser 70 has the inner cylindrical member 78 disposed coaxial or concentric to cylindrical member 78. Sidewalls of each of the cylindrical members can have a pore diameter in a range of 1-200 microns, preferably 1-50 microns and more preferably 5-20 microns. A proximate end of the inner cylindrical member is coupled to an inlet port 72a which is fed an air ozone mixture from pump 36. The microporous diffuser also includes an end cap 74 which in combination secures distal ends of the cylinders 76 and 78. The combination of the inlet cap 72 and end cap 74 seals the microporous diffuser permitting liquid and gas to escape by the porous construction of sidewalls of the microporous diffusers.

Referring now to FIGS. 6A, 6B, construction details for the elongated cylindrical members for the microporous diffusers 50, 70 are shown. As shown in FIG. 6A, sidewalls of the members can be constructed from a metal or a plastic support layer 91 having large (as shown) or fine perforations 91a over which is disposed a layer of a sintered i.e., heat fused microscopic particles of plastic. The plastic can be any hydrophobic material such as polyvinylchloride, polypropylene, polyethylene, polytetrafluoroethylene, high density polyethylene (HDPE) and ABS. The support layer 91 can have fine or coarse openings and can be of other types of materials. FIG. 6B shows an alternative arrangement 94 in which sidewalls of the members are formed of a sintered i.e., heat fused microscopic particles of plastic. The plastic can be any hydrophobic material such as polyvinylchloride, polypropylene, polyethylene, polytetrafluoroethylene, high density polyethylene (HDPE) and alkylbenzylsulfonate (ABS).

The fittings (i.e., the inlets in FIGS. 4A, 5A can be threaded and are attached to the inlet cap members by epoxy, heat fusion, solvent or welding with heat treatment to remove volatile solvents or other approaches. Standard threading can be used for example NPT (national pipe thread) or box thread e.g., (F480). The fittings thus are securely attached to the microporous diffusers in a manner that insures that the microporous diffusers can handle pressures that are encountered with injecting of the air/ozone and liquid.

Referring to FIGS. 7A-7B, an alternate microporous diffuser 90 is shown. The microporous diffuser 90 includes a first cylindrical member 96

comprised of a hydrophobic material which provides an outer cylindrical shell for the microporous diffuser 90. The cylindrical member 96 has a sidewall 96a that is comprised of a large plurality of micro pores. A

5 proximate end of cylindrical member 96 is coupled to a first inlet port 92a provided from a first inlet cap 92 and a distal end of the cylindrical member 96 is coupled to an end cap 94. The end cap 94 in conjunction with cap 92 seals the ends of the microporous diffuser 90.

10 Sidewalls of the cylindrical members 96 is provided with a film of a catalysts or reaction promoter or and absorbing material. Examples include a layer 93 of activated carbon that is abraded into the surface or sintered into the surface. Additionally palladized

15 activated carbon could also be used. As explained above the layer 93 can aid in decomposition of the contaminants in the water. Sidewalls of each of the cylindrical members can have a pore diameter in a range of 1-200 microns, preferably 1-50 microns and more preferably 5-20

20 microns.

The use of catalysts supported by absorptive materials such as palladized activated carbon can be particularly effective for compounds that have an absorptive affinity to activated carbon. The compounds

25 such as TCE are concentrated near the release location of the ozone micro bubbles, allowing more efficient reaction for water containing lower concentrations of TCE as explained above. The layer 93 can also be provided on the other embodiments 50, 70 above, e.g., on either or

30 both cylindrical members but preferably on the members that deliver the ozone to the water.

Referring now to FIGS. 8A and 8B, an alternate arrangement of a spring box 110 is shown. The spring box 110 includes a circular container 111 comprised of a sidewall 112 of a durable material such as concrete over which is disposed or attached a water tight lid 113 also comprised of concrete. Within the spring box 110 is provided an inlet port 115a to receive the water from the spring. Within the circular container are disposed a plurality of microporous diffusers such as those shown in conjunction with my issued U.S. Patent No. 5,855,775 which is incorporated herein by reference.

Alternatively, microporous diffusers 50, 70, 90, as described above in conjunction with FIGS. 4A and 4B, FIGS. 5A and 5B, or FIGS. 7A-7B may be used.

In the arrangement shown in FIG. 8A, the microporous diffusers 116 are coupled to a common rotary joint 117 that can provides a gas/ozone feed arrangement 86a which can be fed, for example, from compressor/pump 24 and compressor 28 (FIG. 2). As shown in FIG. 8B, the microporous diffusers are arranged in elevation above the bottom of the spring box 110 within a pool 119 of water provided from the spring or other surface water source. The rotary joint 117 enables the microporous diffusers to be rotated in the water enabling the ozone to more effectively mix with the water. The spring box 110 can include a sand or other matrix 120 containing a reaction promoter e.g., catalyst as mentioned.

The spring box 110 is an ozone reactor vessel in which ozone is pumped into the pool of water through the use of the microporous diffusers. The microporous diffusers 116 are disposed in the water under treatment and transfer ozone into the water in the form of micro

fine or fine bubbles which promote rapid gas/gas/water reactions with volatile organic compounds particularly in the presence of a catalyst or enhancer which may participate in the gaseous phase of the reaction, instead  
5 of solely enhancing dissolved aqueous disassociation and reactions.

In addition, an optional liquid port (not shown) to the rotary joint can be provided to include gas/gas reactions within the gaseous phase as well as  
10 inducing water aqueous phased reactions to achieve an overall decomposition rate within the gaseous phase and the aqueous phase from second water reactions. For example, the use of hydrogen peroxide as a laminate coating on the bubbles can enhance decomposition rates as  
15 mentioned above.

Referring now to FIG. 9, an alternative example of the use of the microporous diffusers 50, 70 is shown. The example shows an injection well to treat subsurface waters of an aquifer. The arrangement includes a well  
20 having a casing with an inlet screen and outlet screen to promote a recirculation of water into the casing and through the surrounding ground area. The casing supports the ground about the well. Disposed through the casing is microporous diffusers e.g., 50 or 70. The injection  
25 well treatment system 120 also includes an air compressor 132, a compressor/pump control mechanism 134, and an ozone (O<sub>3</sub>) generator 136. The air compressor 134 can feed a stream of air into the microporous diffuser 50 whereas, the compressor pump control 134 feeds a stream of air  
30 mixed with ozone (O<sub>3</sub>) from the ozone generator 136 into microporous diffuser to affect substantial removal of the above-mentioned or similar types of contaminants.

Optionally, or in addition thereto, the treatment system 120 can also include a pump 138 that supplies a liquid decontamination agent such as hydrogen peroxide as well as nutrients such as catalyst agents including iron  
5 containing compounds such as iron silicates or palladium containing compounds such as palladized carbon. In addition, other materials such as platinum may also be used.

The treatment system 120 makes use of a gas-gas  
10 reaction of contaminant vapors and ozone (described below) that can be supplemented with a liquid phase reaction. The use of hydrogen peroxide as a thin film coating on the bubbles promotes the decomposition rate by adding a secondary liquid phase reactive interface as  
15 volatile compounds enter the gaseous phase. It also expands the types of compounds that can be effectively removed. Alternatively, the pump control 138 can simply feed water.

In particular, with the microporous diffusers  
20 50 and 70 and use of the optional port to introduce a liquid such as hydrogen peroxide or water into the chamber, the microbubbles are produced in the microporous diffuser by bubbling air/ozone through the central cylinder of the microporous diffusers and into the  
25 surrounding outer regions of the microporous diffusers. At the same time, a liquid is introduced into the microporous diffusers 50, 70 and laminates an outer surface of bubbles formed by the gas. The liquid forms a liquid barrier between the water to be treated and the  
30 inside gas containing air/ozone. This arrangement thus can be injected into a slurry containing a catalyst such as silicate, iron silicate, palladium, palladized carbon

or titanium dioxide to produce rapid reactions to decompose contaminants within the pool of water contained in the spring box 30. The reactions can proceed as set out below.

5           The process uses microfine bubble injection to produce simultaneous extraction/decomposition reactions as opposed to simply creating smaller and smaller sized bubbles for the purpose of injecting into free water. The process involves generation of fine bubbles which can  
10 promote rapid gas/gas/water reactions with volatile organic compounds which a substrate (catalyst or enhancer) participates in, instead of solely enhancing dissolved (aqueous) disassociation and reactions. The production of microbubbles and selection of appropriate  
15 size distribution is provided by using microporous material and a bubble chamber for optimizing gaseous exchange through high surface area to volume ratio and long residence time within the liquid to be treated. The equipment promotes the continuous production of  
20 microbubbles while minimizing coalescing or adhesion.

          The injected air/liquid combination moves as a fluid into the water to be treated. The use of microencapsulated ozone enhances and promotes in-situ stripping of volatile organics and simultaneously  
25 terminates the normal reversible Henry's reaction. The process involves promoting simultaneous volatile organic compounds (VOC) in-situ stripping and gaseous decomposition, with moisture (water) and substrate (catalyst or enhancer). The reaction mechanism is not a  
30 dissolved aqueous reaction. In some cases, with cis- or trans-DCE, the aqueous phase reaction may assist the predominantly gas-phase reaction.

The remote process controller and monitor allows for the capability for sensor feedback and remote communication to the pump control 24 and ozone (or oxygen or both) generator 26 to achieve a certain level of gaseous content (e.g., dissolved oxygen, ozone, or other gas) and rate of mixing to promote efficient reactions. This is done by sensors 39 (FIGS. 3A, 3B) placed in the bubble chambers at certain distances from the microporous diffusers 50, 70. Oxygen content, redox potential, and dissolved VOC concentration of the water can be monitored within the treatment system. The operator can access the information, modify operations and diagnose the condition of the unit by telephone modem or satellite cell phone. This provides on-site process evaluation and adjustment without the need of on-site operator presence.

Appropriately sized microfine bubbles can be generated in a continuous or pulsing manner which allows alternating water/bubble/water/bubble fluid flow. The microfine bubbles substantially accelerate the transfer rate of volatile organic compounds like PCE from aqueous to gaseous state. Reducing the size of the bubbles to microfine sizes, e.g., 5 to 50 microns, can boost extraction rates. These sizes boost exchange rates and do not tend to retard rise time by too small a size. When an oxidizing gas (ozone) is added into the microbubbles, the rate of extraction is enhanced further by maintaining a low interior (intrabubble) concentration of PCE, while simultaneously degrading the PCE by a gas/gas/water reaction. The combination of both processes acting simultaneously provides a unique rapid removal system which is identified by a logarithmic rate of removal of PCE, and a characteristic ratio of

efficiency quite different from dissolved (aqueous) ozone reactions. The compounds commonly treated are HVOCs (halogenated volatile organic compounds), PCE, TCE, DCE, vinyl chloride (VC), petroleum compounds (BTEX: benzene, toluene, ethylbenzene, xylenes).

An analysis of the reaction mechanism is set out. Gaseous exchange is proportional to available surface area. With partial pressures and mixtures of volatile gases being held constant, a halving of the radius of bubbles would quadruple (i.e., times) the exchange rate. If, in the best case, a standard well screen creates air bubbles 200 times the size of a medium sand porosity, a microporous diffuser of 5 to 20 micron size creates a bubble 1/10 the diameter and six to ten times the volume/surface ratio as shown in Table 1.

Table 1

Diameter (microns)	Surface Area $4\pi$	Volume $4/3\pi$	Surface Area/Volume
200	124600	4186666	0.03
20	1256	4186	0.3

Theoretically, the microporous bubbles exhibit an exchange rate of ten times the rate of a comparable bubble from a standard ten slot well screen.

Table 2

Surface to Volume (A/V) Ratio Changes As Function of Bubble Size As Bubble Volume Increases

D(i.e.,2r) or h as Fraction of Pore Size	0.1	0.25	0.5	1	2	5	10	20

Sphere	SPHEROID							
Area = $4\pi r^2$	0.0314	0.19625	0.785	3.14	18.8	37.7	69	131
Vol = $4/3\pi r^3$	0.0005	0.00817	0.065	0.53	6.3	15.7	31	62
Ratio	62	24	12	5.9	3	2.4	2.2	2.1

In wastewater treatment, the rate of transfer between gas and liquid phases is generally proportional to the surface area of contact and the difference between the existing concentration and the equilibrium concentration of the gas in solution. Simply stated, if the surface to volume ratio of contact is increased, the rate of exchange also increases as illustrated in Table 2. If, the gas (VOC) entering the bubble (or micropore space bounded by a liquid film), is consumed, the difference is maintained at a higher entry rate than if the VOC is allowed to reach saturation equilibrium. In the case of a halogenated volatile organic carbon compound (HVOC), PCE, gas/gas reaction of PCE to by-products of HCl, CO<sub>2</sub> and H<sub>2</sub>O accomplishes this. In the case of petroleum products like BTEX (benzene, toluene, ethylbenzene, and xylenes), the benzene entering the bubbles reacts to decompose to CO<sub>2</sub> and H<sub>2</sub>O. The normal equation for the two-film theory of gas transfer is:

$$r_m = K_g A (C_g - C) \text{ where:}$$

$r_m$  = rate of mass transfer

$K_g$  = coefficient of diffusion for gas

$A$  = area through which gas is diffusing

$C_g$  = saturation concentration of gas in solution

$C$  = concentration of gas in solution.

The restatement of the equation to consider the inward transfer of phase change from dissolved HVOC to gaseous HVOC in the inside of the bubble would be:

5             $C_s$  = Saturation concentration of gas phase of  
              HVOC or                    VOC in bubble.  
               $C$  = Initial concentration of gaseous phase of  
              HVOC                    or VOC in bubble volume.

10            Soil vapor concentrations are related to two  
              governing systems: water phase and (non-aqueous) product  
              phase. Henry's and Raoult's Laws are commonly used to  
              understand equilibrium-vapor concentrations governing  
              volatilisation from liquids. When soils are moist, the  
              relative volatility is dependent upon Henry's Law. Under  
              normal conditions (free from product) where volatile  
              organic carbons (VOCs) are relatively low, an equilibrium  
15            of soil, water, and air is assumed to exist. The  
              compound tetrachloroethene (PCE) has a high exchange  
              capacity from dissolved form to gaseous form. If the  
              surface/volume ratio is modified at least ten fold, the  
              rate of removal should be accelerated substantially.

20            FIG. 10 shows a plot of removal rate of PCE for  
              an aqueous solution equivalent to 120 ppb, over differing  
              bubble sizes. The air volume and water volume is held  
              constant. The only change is the diameter of bubbles  
              passed through the liquid from air released from a  
25            diffuser.

              Ozone is an effective oxidant used for the  
              breakdown of organic compounds in water treatment. The  
              major problem in effectiveness is that ozone has a short  
              lifetime. If ozone is mixed with sewage containing water  
30            above ground, the half-life is normally minutes. Ozone  
              reacts quantitatively with PCE to yield breakdown  
              products of hydrochloric acid, carbon dioxide, and water.

              To offset the short life span, the ozone is  
              injected with microporous diffusers, enhancing the

selectiveness of action of the ozone. By encapsulating the ozone in fine bubbles, the bubbles would preferentially extract volatile compounds like PCE from the mixtures of soluble organic compounds they encountered. With this process, volatile organics are selectively pulled into the fine air bubbles. Gas entering a small bubble of volume  $(4\pi r^3)$  increases until reaching an asymptotic value of saturation. If we consider the surface of the bubble to be a membrane, a first order equation can be written for the monomolecular reaction of the first order. The reaction can be written

$$\frac{dx}{dt} = K(Q - X)$$

as follows:

where X is the time varying concentration of the substance in the bubble, Q is the external concentration of the substance, and K is the absorption constant.

$$X = Q(1 - e^{-Kt})$$

If at time  $t = 0$ ,  $X = 0$ , then:

$$K = \frac{dx/dt}{Q - X}$$

The constant K is found to be:

By multiplying both numerator and denominator

$$K = \frac{v dx/dt}{v(Q - X)}$$

by V, the volume of the bubble, we obtain

which is the ratio between the amount of substance entering the given volume per unit time and quantity  $V(Q-X)$  needed to reach the asymptotic value. By analyzing the concentration change within the fine bubbles sent through a porous matrix with saturated (water filled) solution interacting with the matrix (sand), and determining the rate of decomposition of the products (TCE + ozone = CO<sub>2</sub> + HCl) and (Benzene + ozone = CO<sub>2</sub> + HOH), the kinetic rates of reaction can be characterized.

The rate which the quantity  $k_1QV$  of the substance flows in one unit of time from aqueous solution into the bubble is proportional to Henry's Constant. This second rate of decomposition within the bubble can be

$$\frac{dx}{dt} = k_1Q - k_2X$$

considered as  $k_1$ , a second rate of reaction ( $-k_2X$ ), where

$$X = \frac{k_1}{k_2}Q$$

and, at equilibrium, as  $dx/dt = 0$ , gives

However, if the reaction to decompose is very rapid, so  $-k_2X$  goes to zero, the rate of reaction would maximize  $k_1Q$ , i.e., be proportional to Henry's Constant and maximize the rate of extraction since VOC saturation is not occurring within the bubbles.

The combination of microbubble extraction and ozone degradation can be generalized to predict the volatile organic compounds amenable to rapid removal. The efficiency of extraction is directly proportional to Henry's Constant. Multiplying the Henry's Constant (the

partitioning of VOCs from water to gas phase) times the reactivity rate constant of ozone for a particular VOC yields the rate of decomposition expected by the microbubble process.

5           The concentration of HVOC expected in the bubble is a consequence of rate of invasion and rate of removal. In practice, the ozone concentration is adjusted to yield 0 concentration at the time of arrival

$$r_{voc} = -K_L a_{voc} (C - C_L)$$

at the surface.

10

where:

$f_{voc}$  = rate of VOC mass transfer, ( $\mu\text{g}/\text{ft}^3 \cdot \text{h}$ )

$(K_L a)_{voc}$  = overall VOC mass transfer coefficient, (1/h)

15

$C$  = concentration of VOC in liquid

$C_L$  = saturation concentration of VOC in liquid  
 $\mu\text{g}/\text{ft}^3$  ( $\mu\text{g}/\text{m}^3$ )

20           The saturation concentration of a VOC in wastewater is a function of the partial pressure of the VOC in the atmosphere in contact with the wastewater.

$$\frac{C_g}{C_L} = H_c \text{ thus, } C_g = H_c \cdot C_L$$

25            $C_g$  = concentration of VOC in gas phase  $\mu\text{g}/\text{ft}^3$   
( $\mu\text{g}/\text{m}^3$ )

$C_L$  = saturation concentration of VOC in liquid  
 $\mu\text{g}/\text{ft}^3$  ( $\mu\text{g}/\text{m}^3$ )

$H_c$  = Henry's Constant

The rate of decomposition of an organic compound  $C_g$  (when present at a concentration  $(C)$  by ozone

$$-\left(\frac{dC_g}{dt}\right)_{O_3} = K_{o_c}(O_3)(C_g)$$

can be formulated by the equation:

5 or, after integration for the case of a batch reactor:

$$-\ln\left(\frac{C_{g_{end}}}{C_{g_o}}\right) = K_{o_c}(O_3)t \quad (\text{equation 2})$$

$$\begin{aligned} (C_g)_{end} &= C_o e^{-K_{o_c}(O_3)t} \\ \frac{(C_g)_{end}}{(C_g)_o} &= e^{-K_{o_c}(O_3)t} \end{aligned}$$

10

where

15  $(O_3)$  = concentration of ozone averaged over the reaction time  $(t)$

$(C_g)_o$  = halocarbon initial concentration

$(C_g)_{end}$  = halocarbon final concentration

20 Substituting:

$$\begin{aligned}
 r_m &= K_g A (C_g - C) && \text{From Henry's Law:} \\
 r_m &= K_g A ((H_g \cdot C_g) - C) && C_g = H_c \cdot C_g \text{ (equation 3)} \\
 r_m &= K_g Z ((H_g \cdot C_g) - C) && \text{With ozone} \\
 r_m &= K_g Z ((H_c \cdot C_g) - C - K_o (O_3) (C_g)) && \\
 5 \quad & (H_g \cdot C) - K_o (O_3) (C_g) = 0 && \text{(equation 4)}
 \end{aligned}$$

Rate of decomposition is now adjusted to equal the total HVOC entering the bubble.

$$\text{SET: } (H_c \cdot C_g) = K_o (O_3) (C_g) \quad \text{(equation 5)}$$

10 therefore surface concentration = 0

This condition speeds up the rate of extraction because the VOC never reaches equilibrium or saturation in the bubble.

15 Table 4 gives the Henry's Constants ( $H_c$ ) for a selected number of organic compounds and the second rate constants ( $R_2$ ) for the ozone radical rate of reaction in solely aqueous reactions where superoxide and hydroxide reactions dominate. The third column presents rates of removal process.

20

TABLE 4  
REMOVAL RATE COEFFICIENTS

Organic Compound	Ozone Aqueous Second Order Rate Constant (a.) ( $M^{-1} SEC^{-1}$ )	Henry's Constant (b.)	Rate Removal Coefficient ( $\tau$ ) (c.)
Benzene	2	$5.59 \times 10^3$	0.06
Toluene	14	$6.37 \times 10^3$	0.07
Chlorobenzene	0.75	$3.72 \times 10^3$	0.013
Dichloroethylene	110	$7.60 \times 10^3$	0.035
Trichloroethylene	17	$9.10 \times 10^3$	0.05
Tetrachloroethylene	0.1	$25.9 \times 10^3$	0.06
Ethanol	0.02	$.04 \times 10^3$	0.0008

a) From Hoigne and Bader, 1983. "Rate of Constants of Direct Reactions of Ozone with Organic and Inorganic Compounds in Water -I. Nondissociating Compounds" Water Res/ 17:173-184.

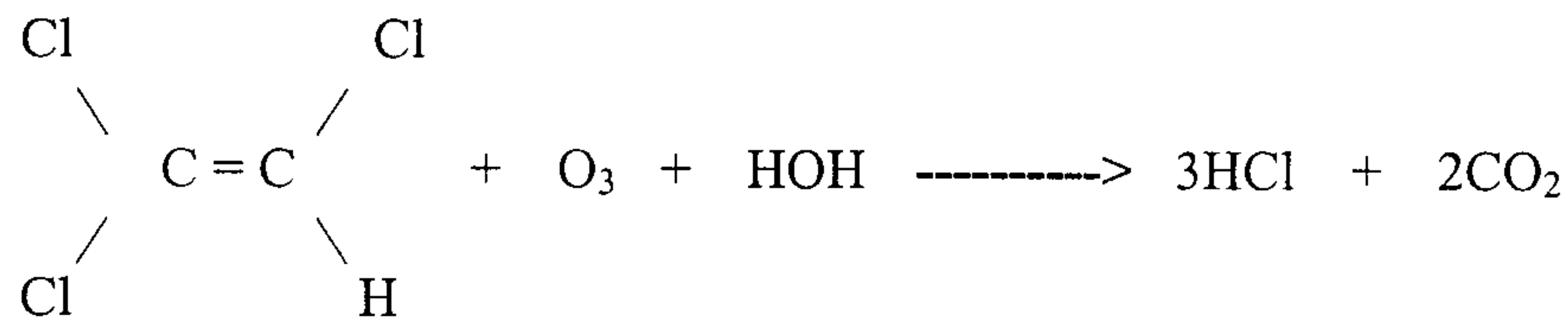
5 b) From EPA 540/1-86/060, Superfund Public Health Evaluation Manual EPA 540/1-86/060 (OSWER Directive 9285.4-1) Office of Emergency and Remedial Response, Office of Solid Waste and Emergency Response.

c) See US Patent 5,855,775.

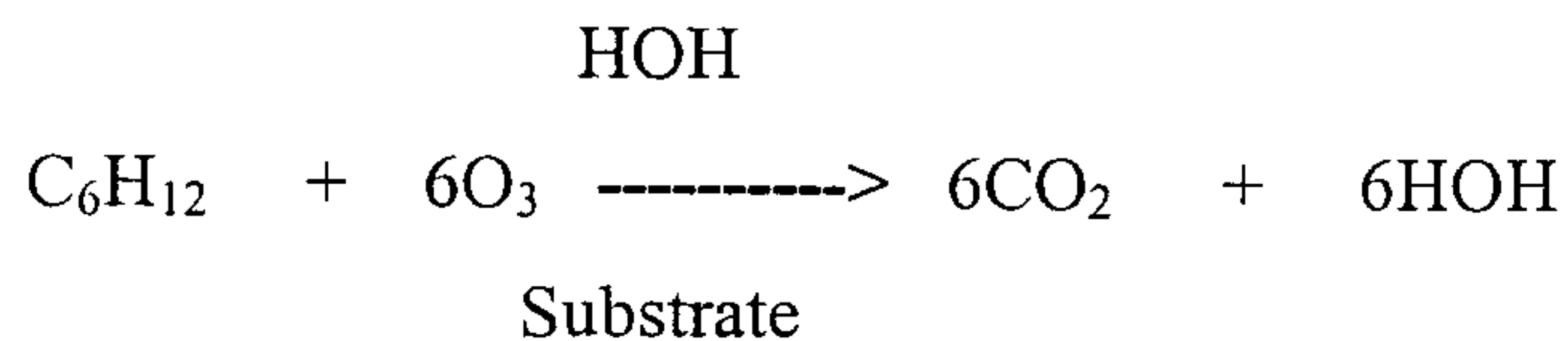
10 The rapid removal rate of this process does not follow Hoigne and Bader (1983) rate constants. However, there is a close correlation to Henry's Constant as would be expected from equation 5. The presence of the substrate (sand) and moisture is necessary to complete  
 15 the reaction. The active ingredient in the sand matrix appears to be an iron silicate. The breakdown products include CO<sub>2</sub> and dilute HCl.

Two sets of equations are involved in the reactions:

20 Dissolved Halogenated Compounds



Dissolved Petroleum Distillates



Exemplary compounds are normally unsaturated (double bond), halogenated compounds like PCE, TCE, DCE, Vinyl Chloride, EDB; or aromatic ring compounds like benzene derivatives (benzene, toluene, ethylbenzene, xylenes). Also, pseudo Criegee reactions with the substrate and ozone appear effective in reducing certain saturated olefins like trichloro alkanes (1,1,-TCA), carbon tetrachloride (CCl<sub>4</sub>), chloroform and chlorobenzene, for instance.

The following characteristics of the contaminants appear desirable for reaction:

Henry's Constant:	10 <sup>-2</sup> to 10 <sup>-4</sup> m <sup>3</sup>
.atm/mol	
Solubility:	10 to 20,000
mg/l	
Vapor pressure:	1 to 3000 mmhg
Saturation concentration:	5 to 9000 g/m <sup>3</sup>

#### Absorption-Destruction

Absorptive substrates like activated carbon and certain resins serve to remove dissolved volatile organic carbon compounds by absorption to the surface. The active surface of particles contain sites which the compounds attach to. The surface absorption is usually mathematically modeled by use of a Langmuir or Freunlich set of equations for particular sizes of particles or total surface area if the material is presented in cylinders or successive plates.

The derivation of the Langmuir isotherm stipulated a limited number of absorption sites on the surface of the solid. The absorption of a solute on the surface necessitates the removal of a solvent molecule. An equilibrium is then reached between the absorbed

fraction and the remaining concentration in solution. If  
a continual gas phase of microbubbles is being released  
from a porous surface, can remove the absorbed molecule  
and decompose it, the reaction would be moved along much  
5 faster than in aqueous phase without the collecting

$$Q_1 = \frac{K_{L1} C_{L1}}{1 + K_{L1} C_{L1}}$$

surface.

$Q_1$  = fractional surface coverage of solute

$K_{L1}$  = equilibrium constant

$C_{L1}$  = solute concentration

10

#### Other Embodiments

It is to be understood that while the invention  
has been described in conjunction with the detailed  
description thereof, the foregoing description is  
15 intended to illustrate and not limit the scope of the  
invention, which is defined by the scope of the appended  
claims. Other aspects, advantages, and modifications are  
within the scope of the following claims.

What is claimed is:

1. An apparatus for treatment of contaminated water comprises:
  - 5 a container divided into at least two chambers by a wall that partially separates the two chambers, the containing having an inlet at a first one of the chambers and an outlet at a second one of the chambers;
    - a first microporous diffuser disposed in a  
10 first one of the chambers of the container and arranged to receive a decontaminating gaseous agent;
    - a second microporous diffuser disposed in a second one of the chambers and arranged to receive air.
- 15 2. The apparatus of claim 1 wherein the first microporous diffuser produces bubbles coated with a laminate of a liquid decontamination agent.
3. The apparatus of claim 1 further comprising:
  - 20 a ozone generator, to supply ozone as the decontaminating gaseous agent, coupled to the first microporous diffuser.
4. The apparatus of claim 3 further comprising a  
25 liquid source also coupled to the first microporous diffuser to produce bubbles of ozone/air with a liquid laminate over the bubbles.
5. The apparatus of claim 4 wherein the liquid is  
30 a liquid decontaminator such as hydrogen peroxide.

6. The apparatus of claim 1 wherein the second microporous diffuser arranged to receive air provides air stripping of any residual gaseous decontaminating agent before water exits the apparatus.
- 5
7. The apparatus of claim 3 wherein the second microporous diffuser is arranged to strip of any residual ozone before water exits the apparatus.
- 10 8. The apparatus of claim 1 wherein the first microporous diffuser is coupled to a plurality of addition micro porous diffusers that are fed the gaseous decontaminating agent.
- 15 9. The apparatus of claim 3 wherein the first microporous diffuser is coupled to a plurality of addition micro porous diffusers that are fed ozone.
10. A spring box apparatus for treatment of  
20 contaminated groundwater comprises:  
a container divided into a plurality of partially closed chambers by a plurality of walls each of which partially separates adjacent chambers;  
a plurality of microporous diffusers arranged  
25 in the corresponding plurality of chambers, with a first portion of the microporous diffusers coupled to a gaseous decontamination agent source, and a remaining portion of the microporous diffuser being coupled to an air source.
- 30 11. The apparatus of claim 10 wherein the microporous diffusers produce bubbles coated with a laminate of a liquid decontamination agent.

12. The apparatus of claim 10 wherein the microporous diffuser comprises:

- 5 a first hollow cylindrical tube having a sidewall comprising a plurality of microscopic openings;
- a second hollow tube having a sidewall having a plurality of microscopic openings, said second tube being disposed through said first tube;
- 10 an end cap to seal ends of said tubes; and  
an inlet cap disposed to provide inlets to interior portions formed by sidewalls of said tubes.

13. The apparatus of claim 11 wherein the spring box further includes a gas distributor that is coupled to  
15 a inlet that feed the decontamination gas to the microporous diffuser.

14. The apparatus of claim 12 wherein the inlet cap  
20 includes a first fitting disposed at a central portion thereof that permits the decontamination gas to be injected through the second tube in the microporous diffuser said first fitting coupled to the gas distributor.

25 15. The apparatus of claim 15 wherein the inlet cap has a second fitting disposed to permit a liquid to be injected through a region defined between the first and second tubes of the microporous diffuser.

30 16. The apparatus of claim 12 wherein the region defined between the first and second tubes of the

microporous diffuser is filled with a catalyst suspension material.

17. The apparatus of claim 16 wherein the catalyst suspension are glass beads or silica elements.

18. The apparatus of claim 14 wherein a catalyst is disposed in the glass beads or silica, said catalyst containing iron.

10

19. The apparatus of claim 15 wherein within the spring box is a layer of an abrasive material that holds a catalyst or reaction promoter.

15 20. The apparatus of claim 12 wherein the first and second tubes are comprised of heat fused microscopic porous particles.

21. The apparatus of claim 20 wherein the tubes are further comprised of a support material including a cylinder of a metal having a plurality of openings to which the heat fused microporous plastic particles are adhered to.

25 22. The microporous diffuser of claim 19 wherein the heat fused fine microporous particles are comprised of a plastic selected from the group consisting of polyvinylchloride, polypropylene, polyethylene, polytetrafluoroethylene, high density polyethylene (HDPE)  
30 and alkylbenzylsulfonate (ABS) or a ceramic.

23. The apparatus of claim 10 wherein the container is constructed of concrete.

24. The apparatus of claim 10 wherein the container  
5 is an airtight closed container constructed of concrete.

25. A method of treating groundwater received from a spring comprises:

introducing the groundwater into a spring box  
10 having at least one microporous diffuser disposed therein, said microporous diffuser delivering microfine bubbles containing air/ozone to the water introduced into the box.

15 26. The method of claim 25 wherein the microporous diffuser delivers the microfine bubbles of air/ozone having a laminate of a liquid over the bubble surface.

27. The method of claim 25 wherein the microporous  
20 diffuser delivers the microfine bubbles of air/ozone having a laminate of a decontaminating liquid over the bubble surface.

28. The method of claim 25 wherein the  
25 decontaminating liquid over the bubble surface is hydrogen peroxide.

29. A method of treating an aquifer or soil formations, comprises:

30 sparging the aquifer or soil formations with a microporous diffuser that delivers hydrogen peroxide as a

surface layer over microfine bubbles including an oxidization gas.

30. The method of claim 29 wherein the microporous  
5 diffuser includes nutrients such as catalyst agents including iron containing compounds such as iron silicates or palladium containing compounds such as palladized carbon and platinum.

10 31. The method of claim 29 wherein the microporous diffuser have absorptive layer over the surface of the diffusers to remove dissolved volatile organic carbon compounds by absorption to the surface.

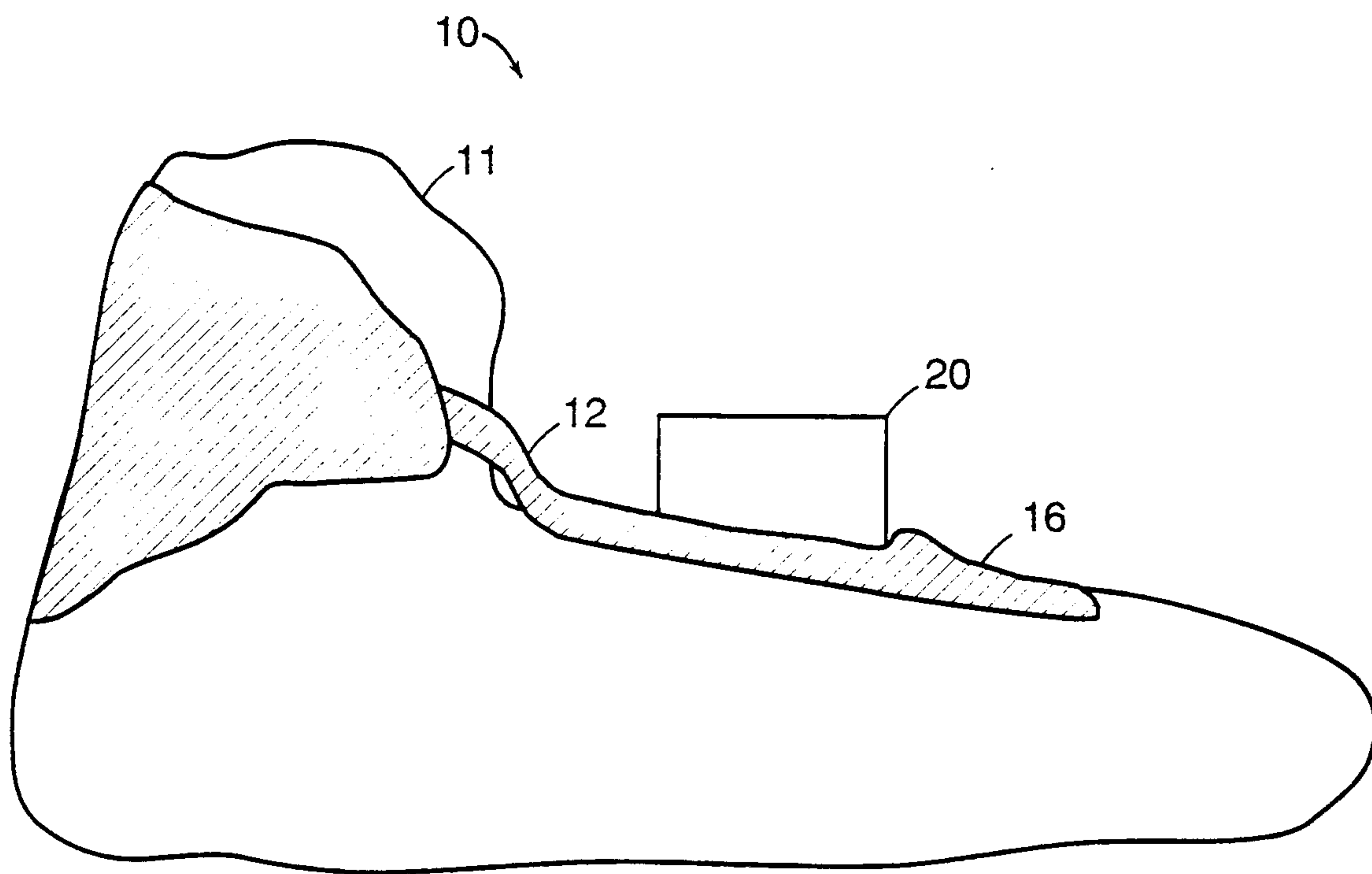


FIG. 1

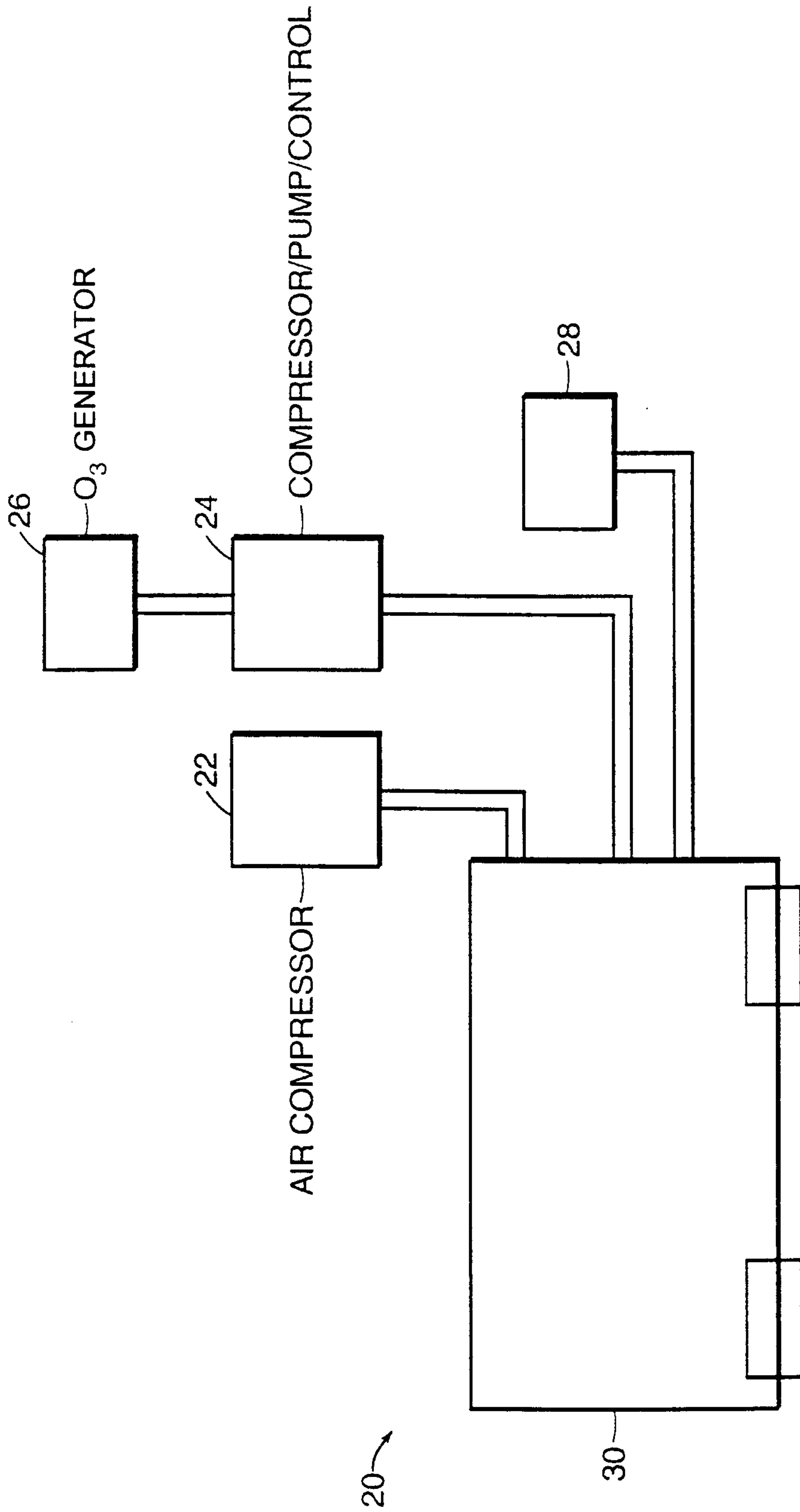


FIG. 2

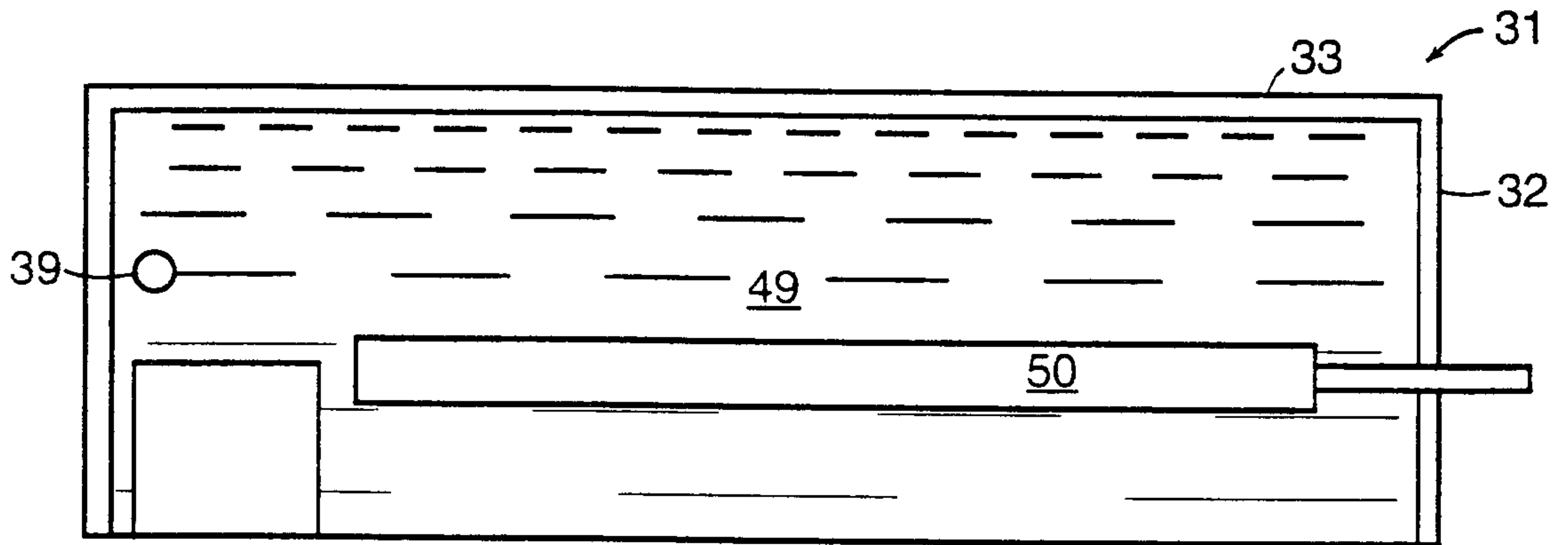


FIG. 3B

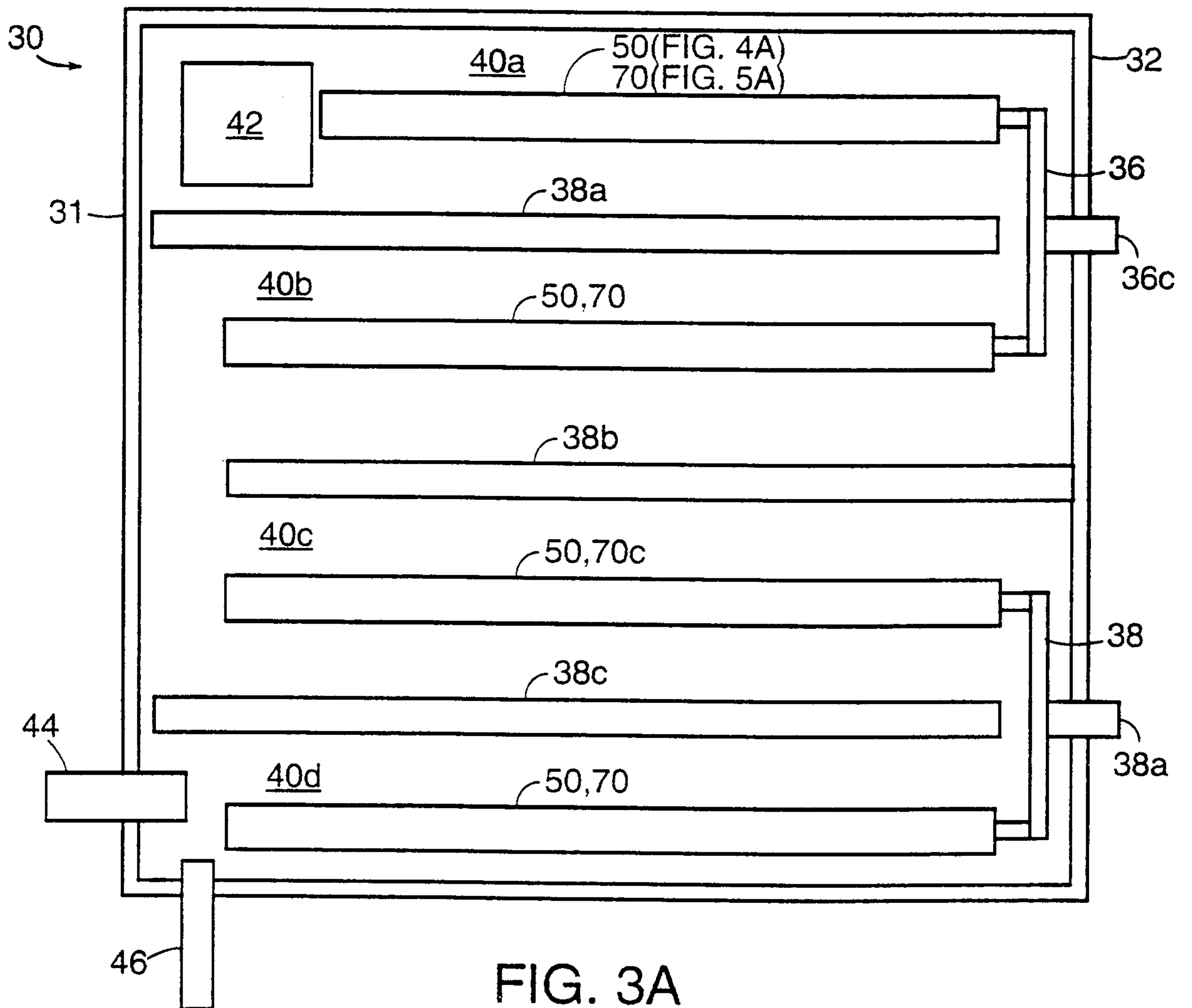


FIG. 3A

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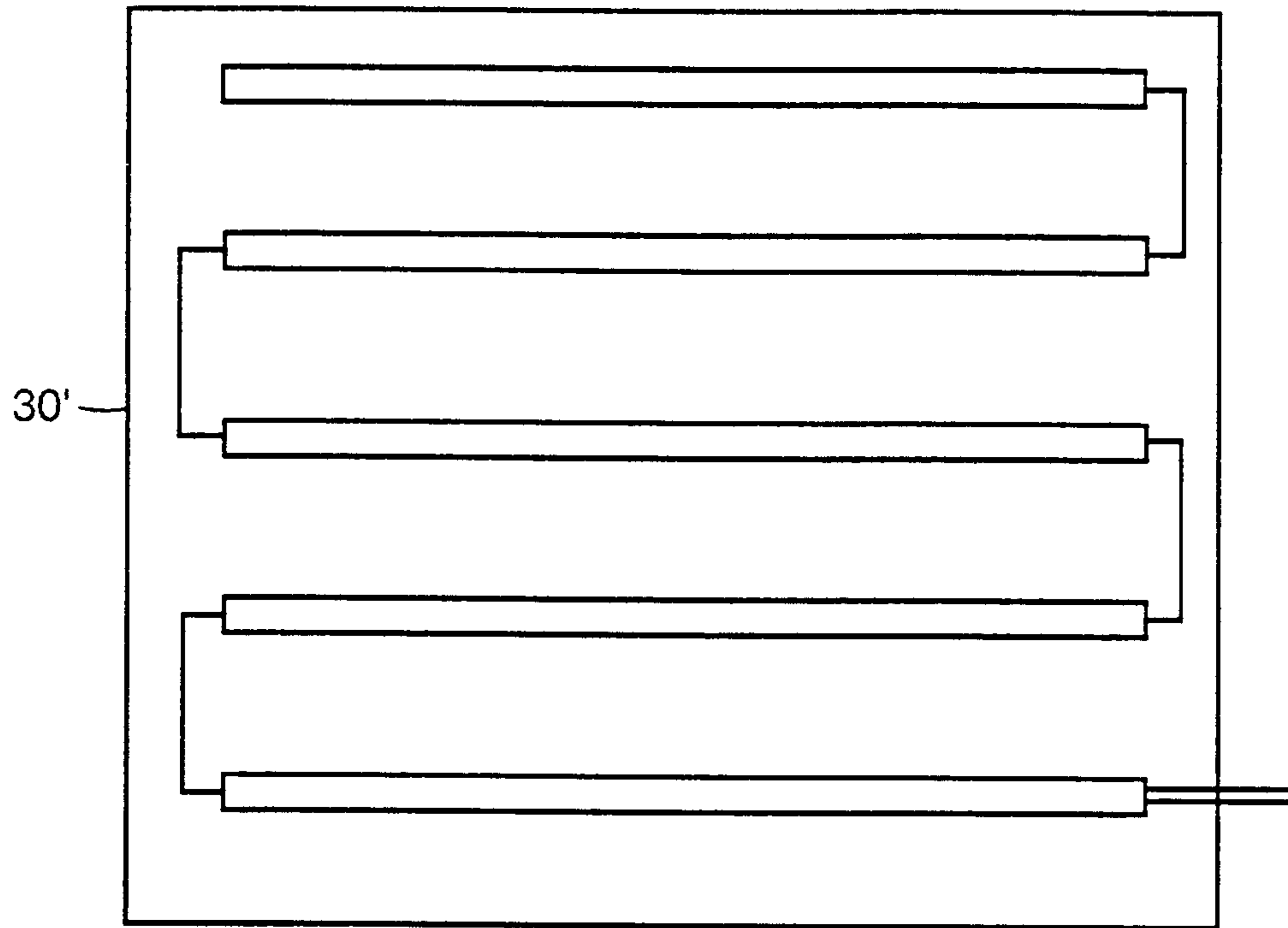


FIG. 3C

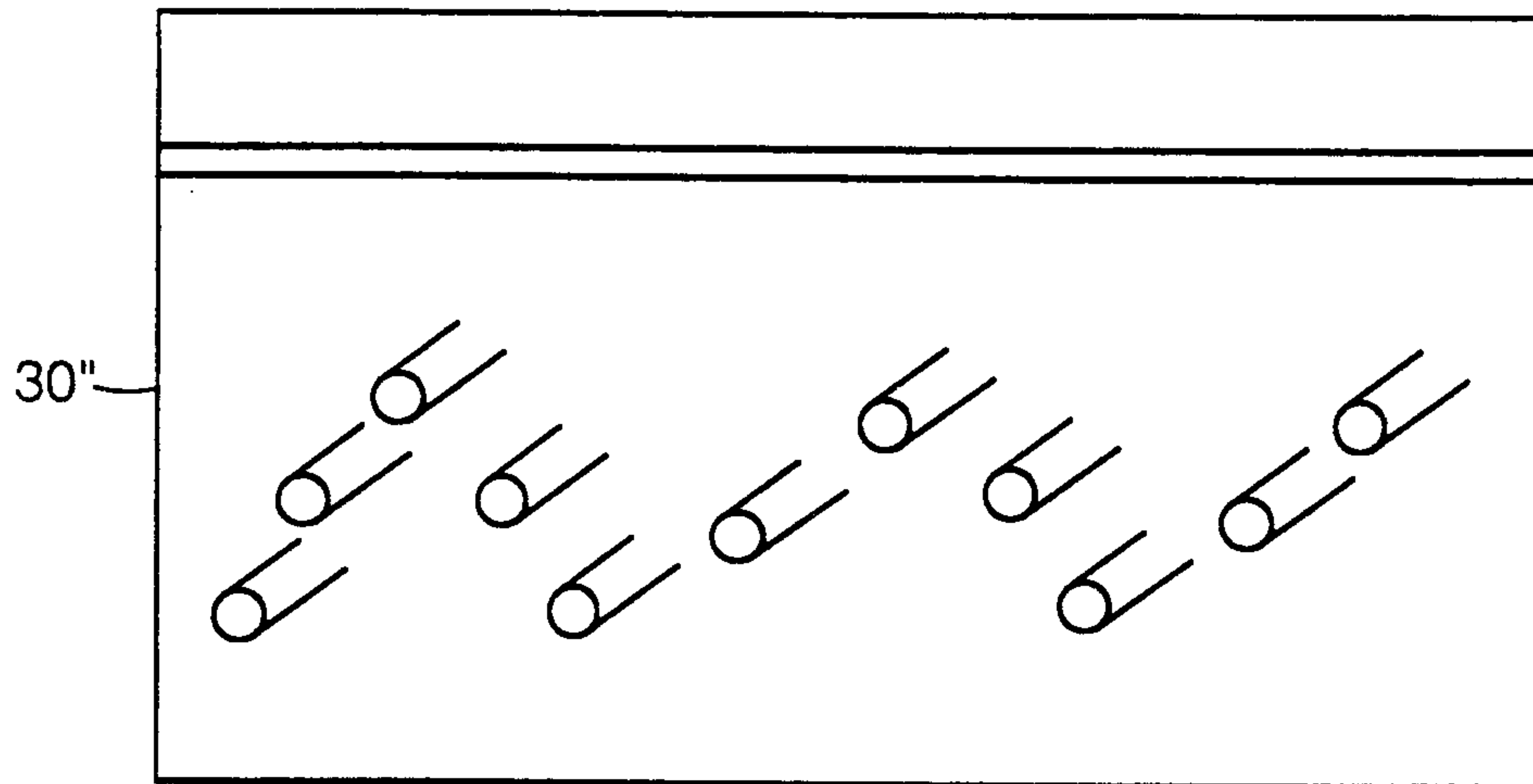


FIG. 3D

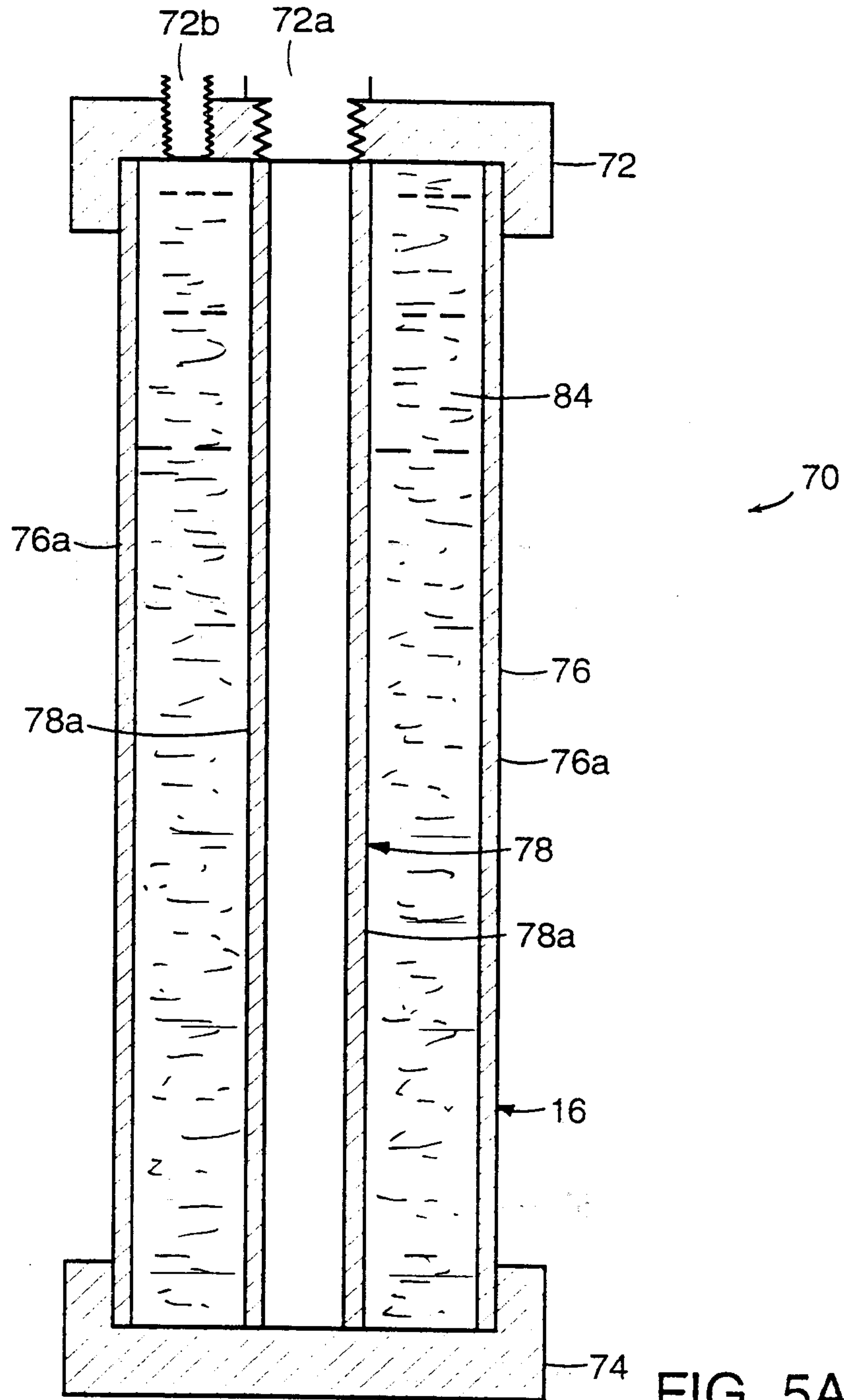


FIG. 5A

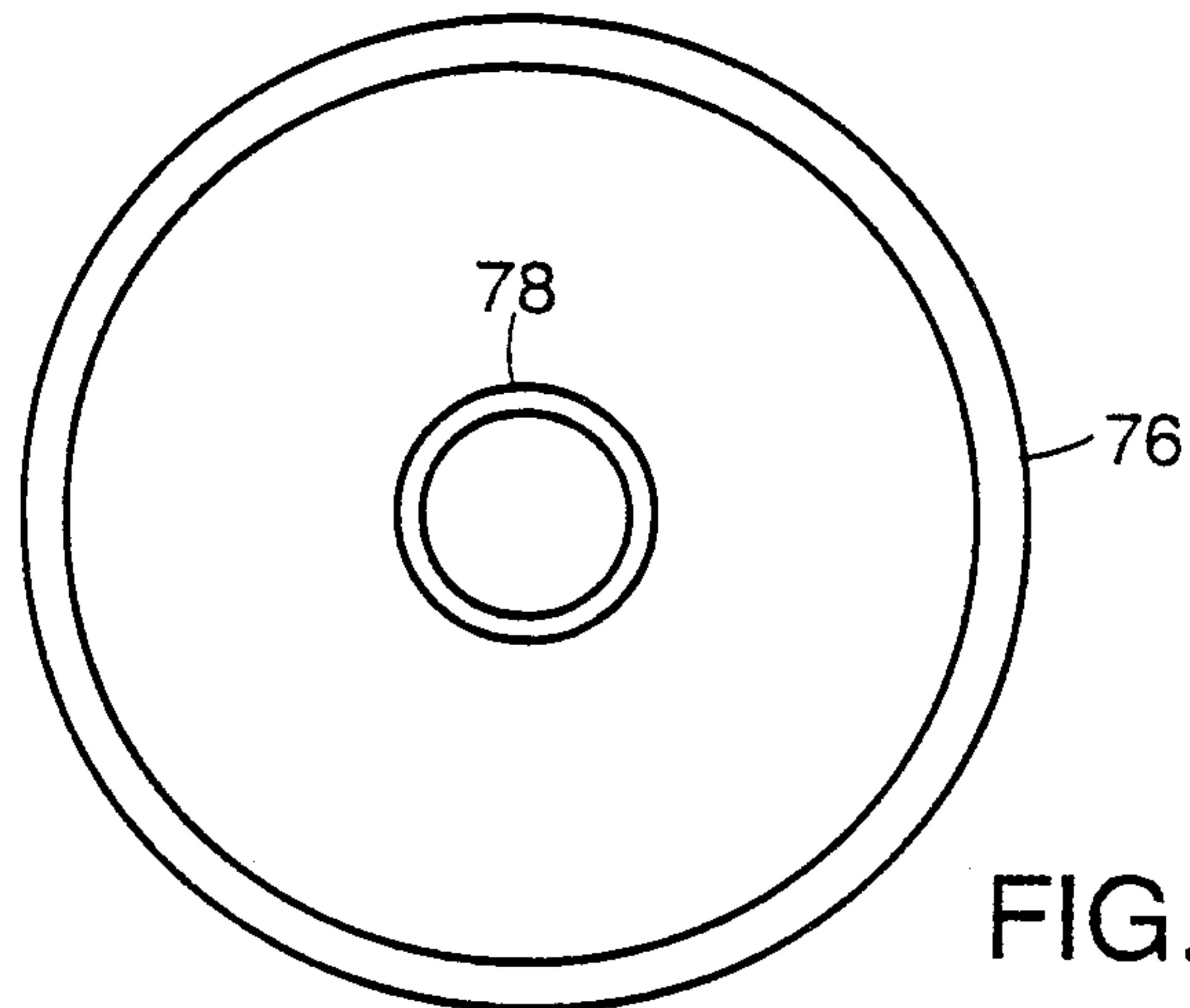


FIG. 5B



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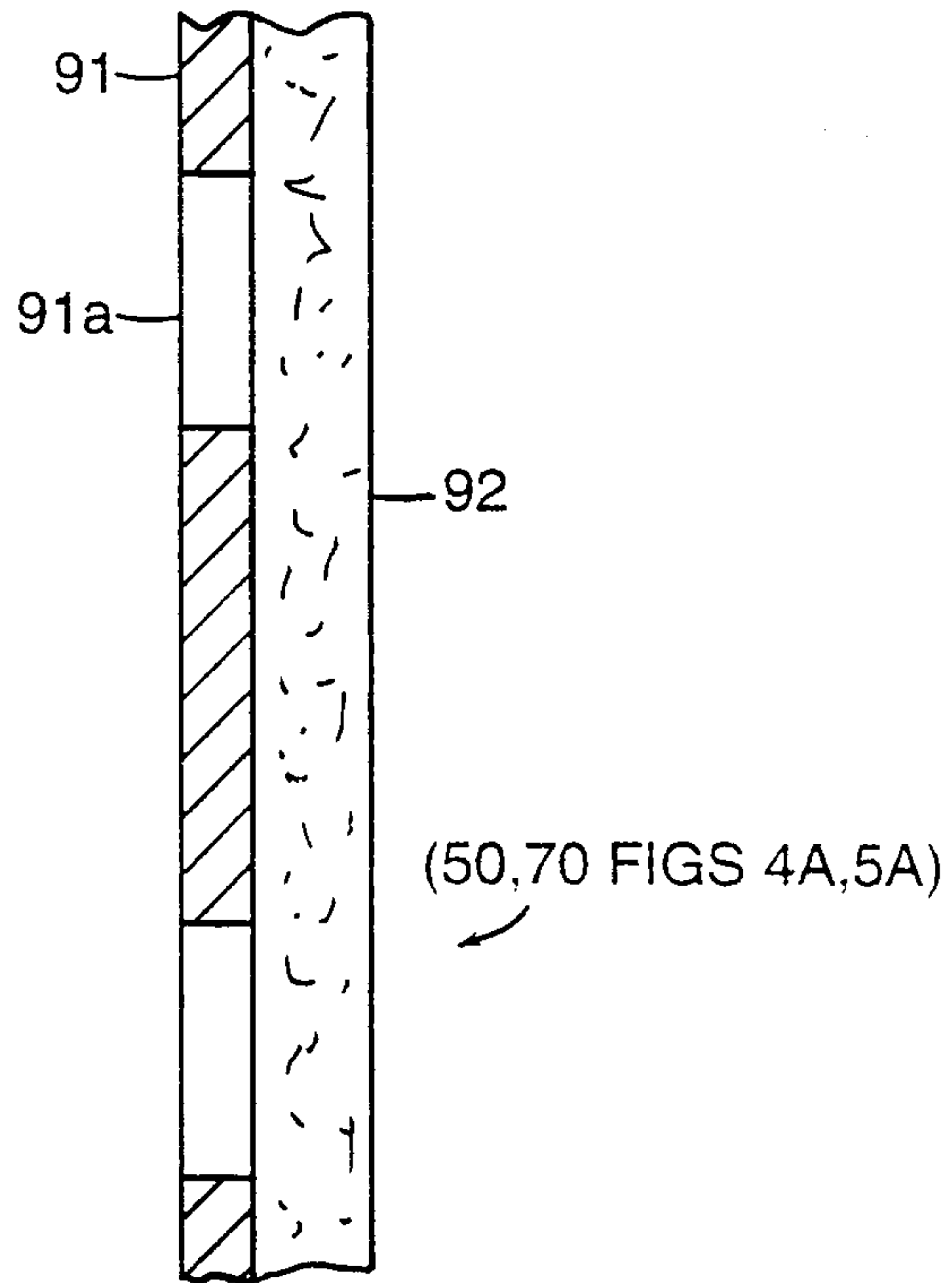


FIG. 6A

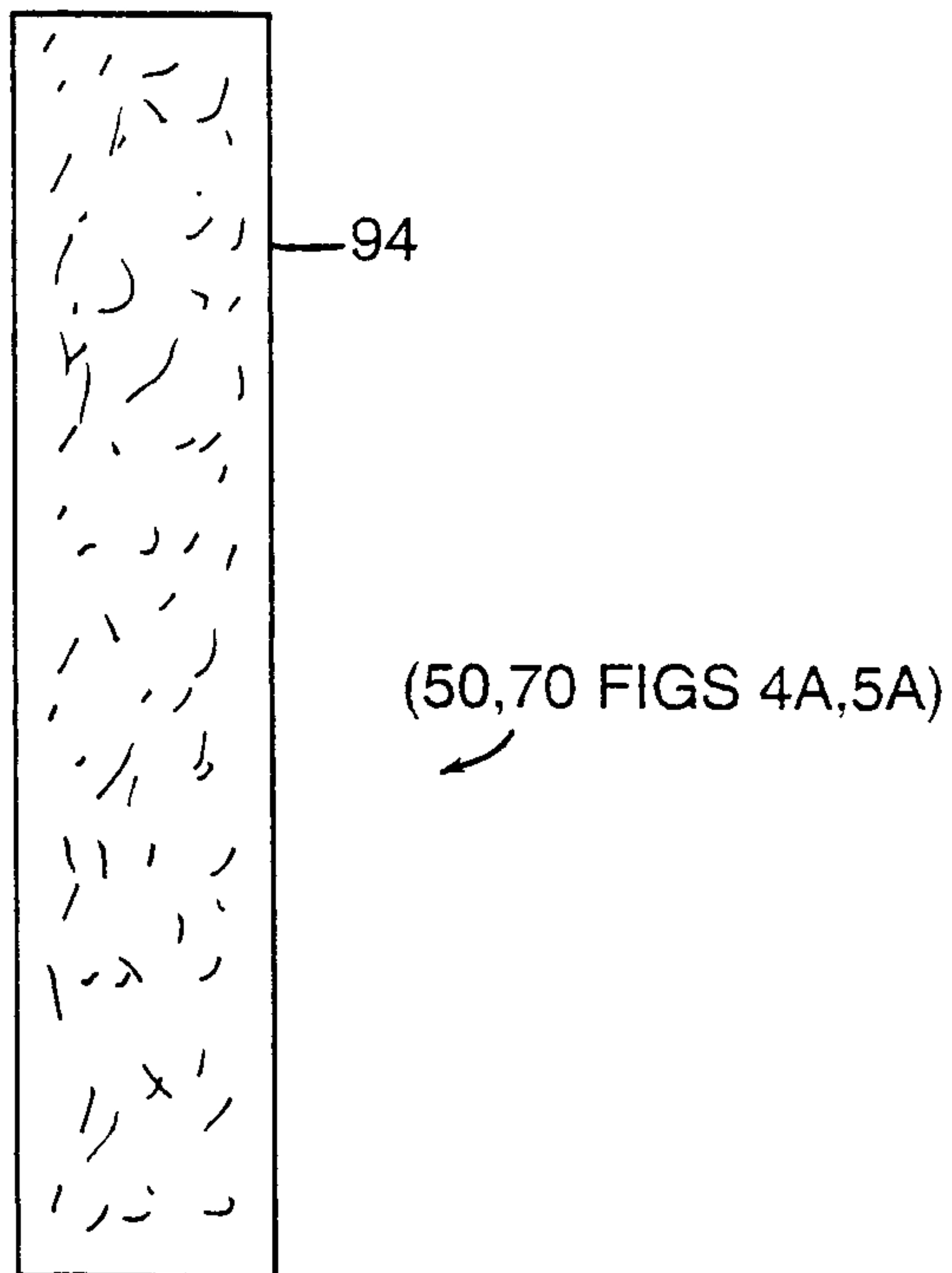


FIG. 6B

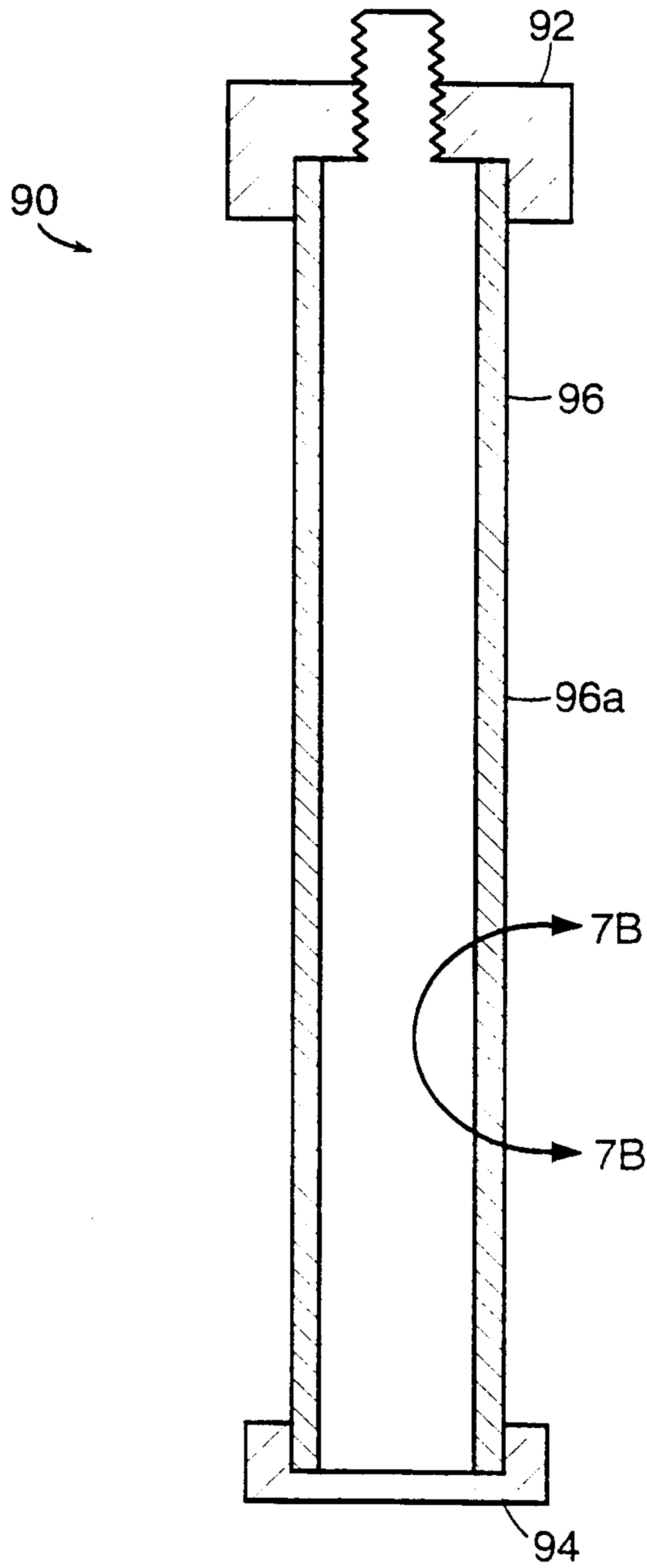


FIG. 7A

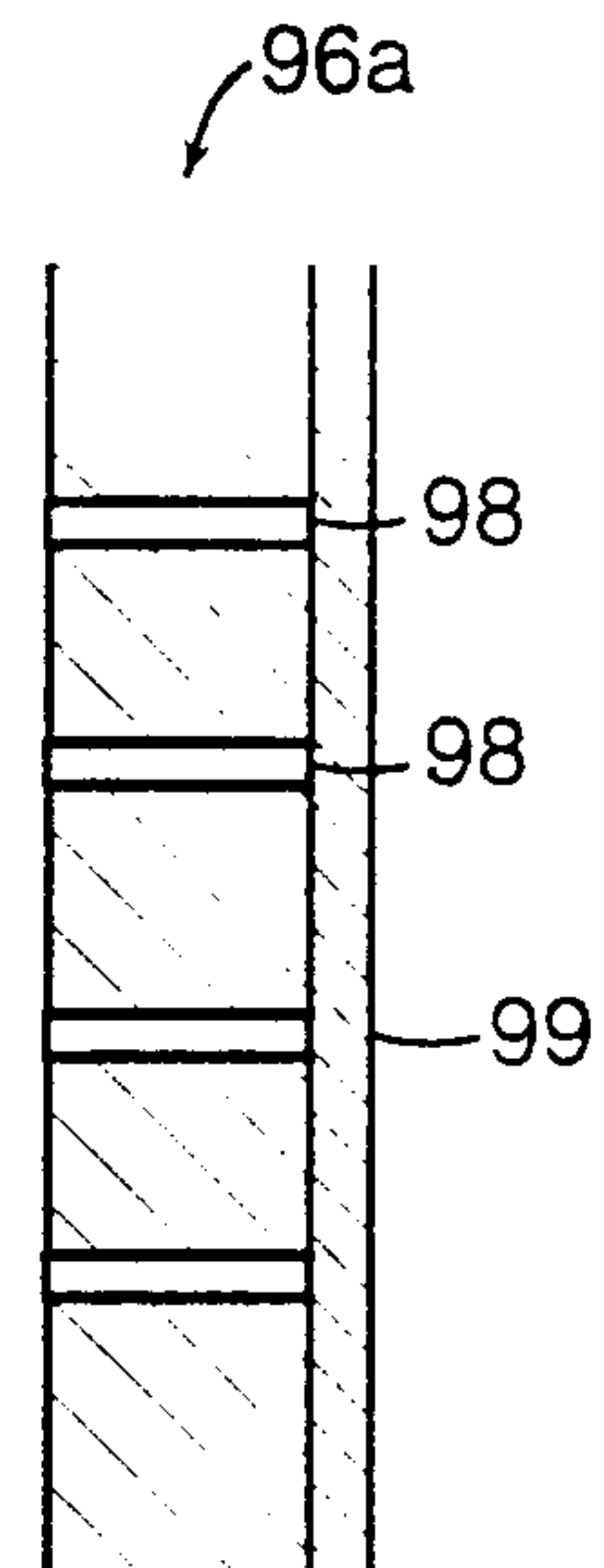


FIG. 7B

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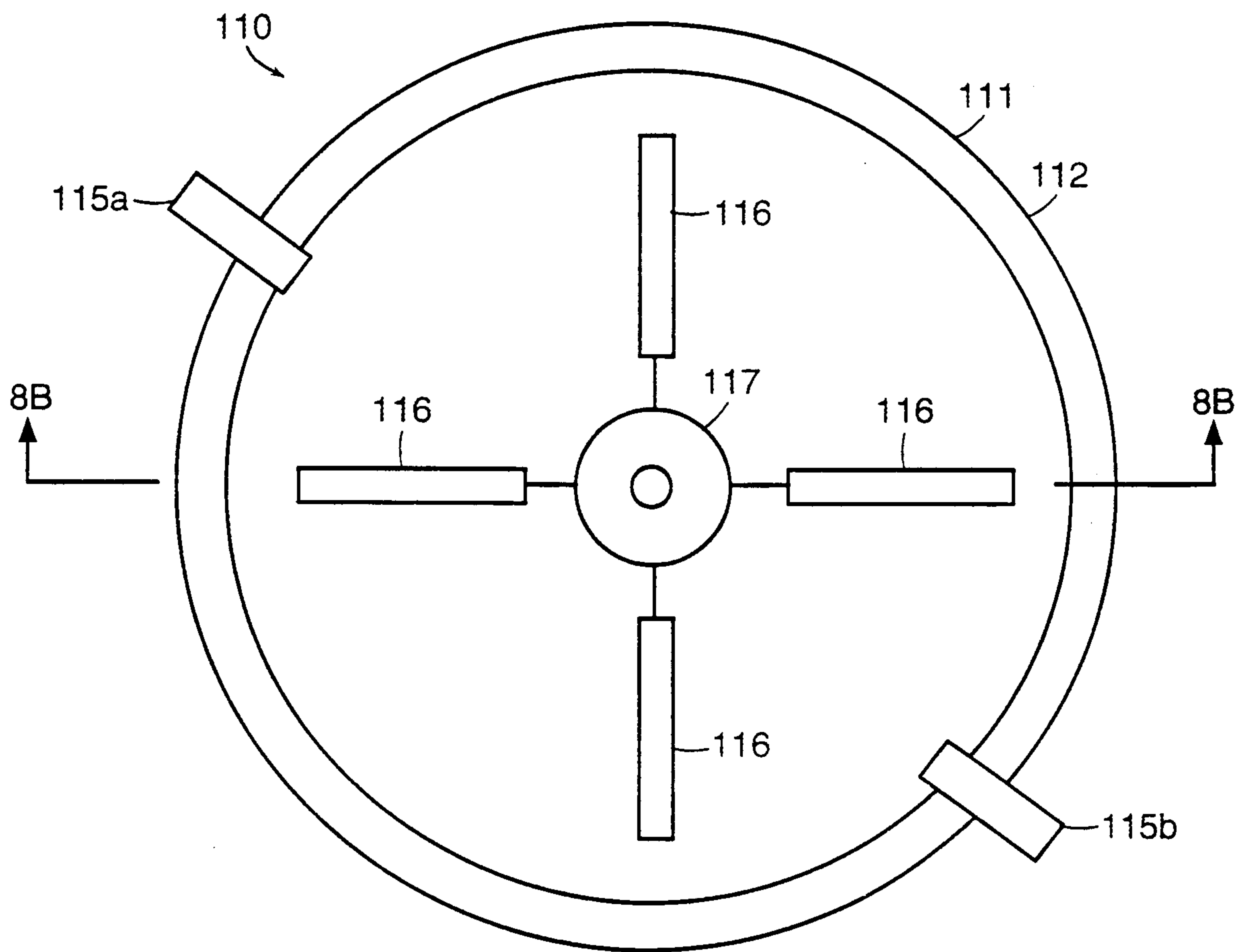


FIG. 8A

10/12

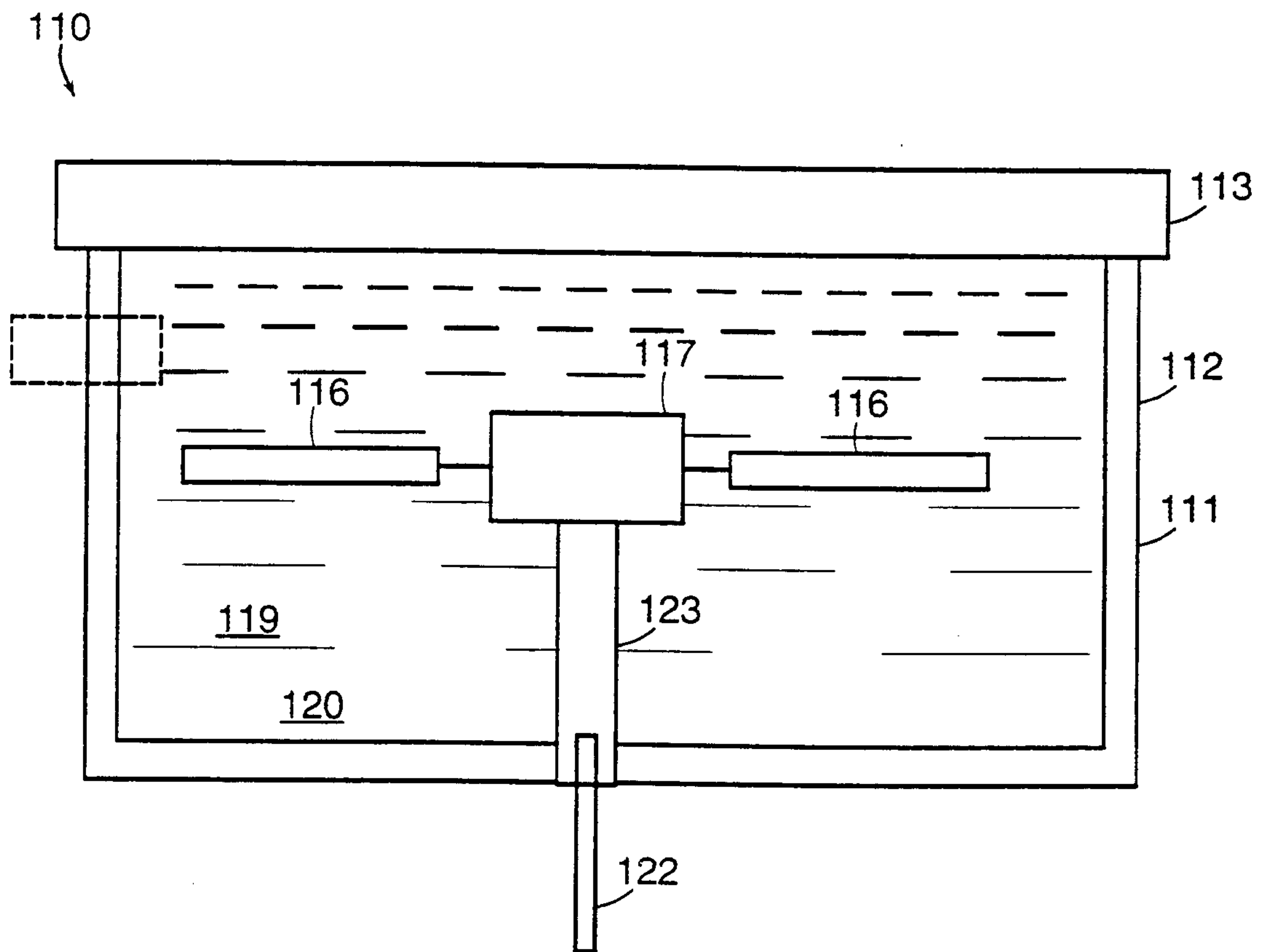


FIG. 8B

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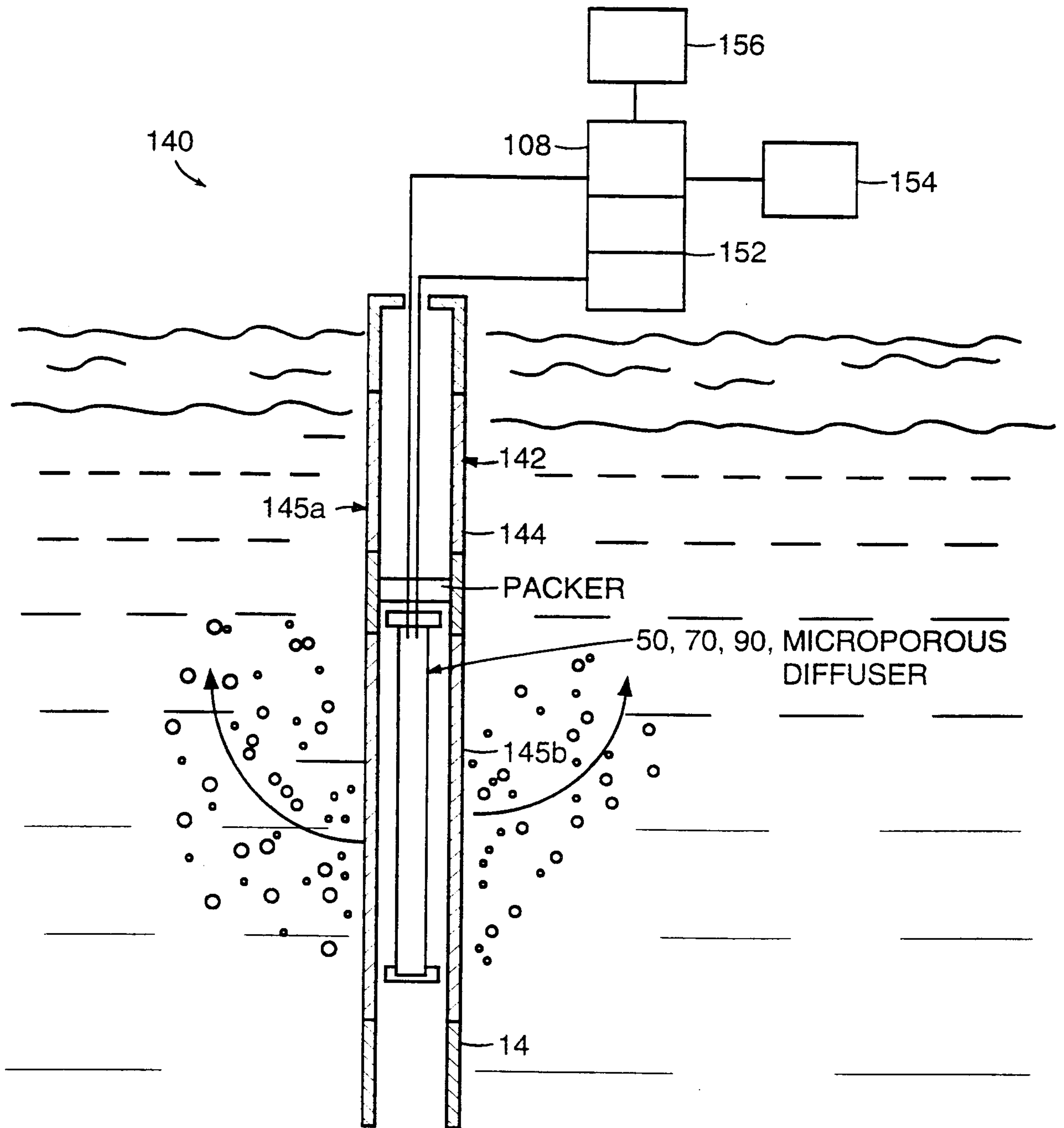


FIG. 9

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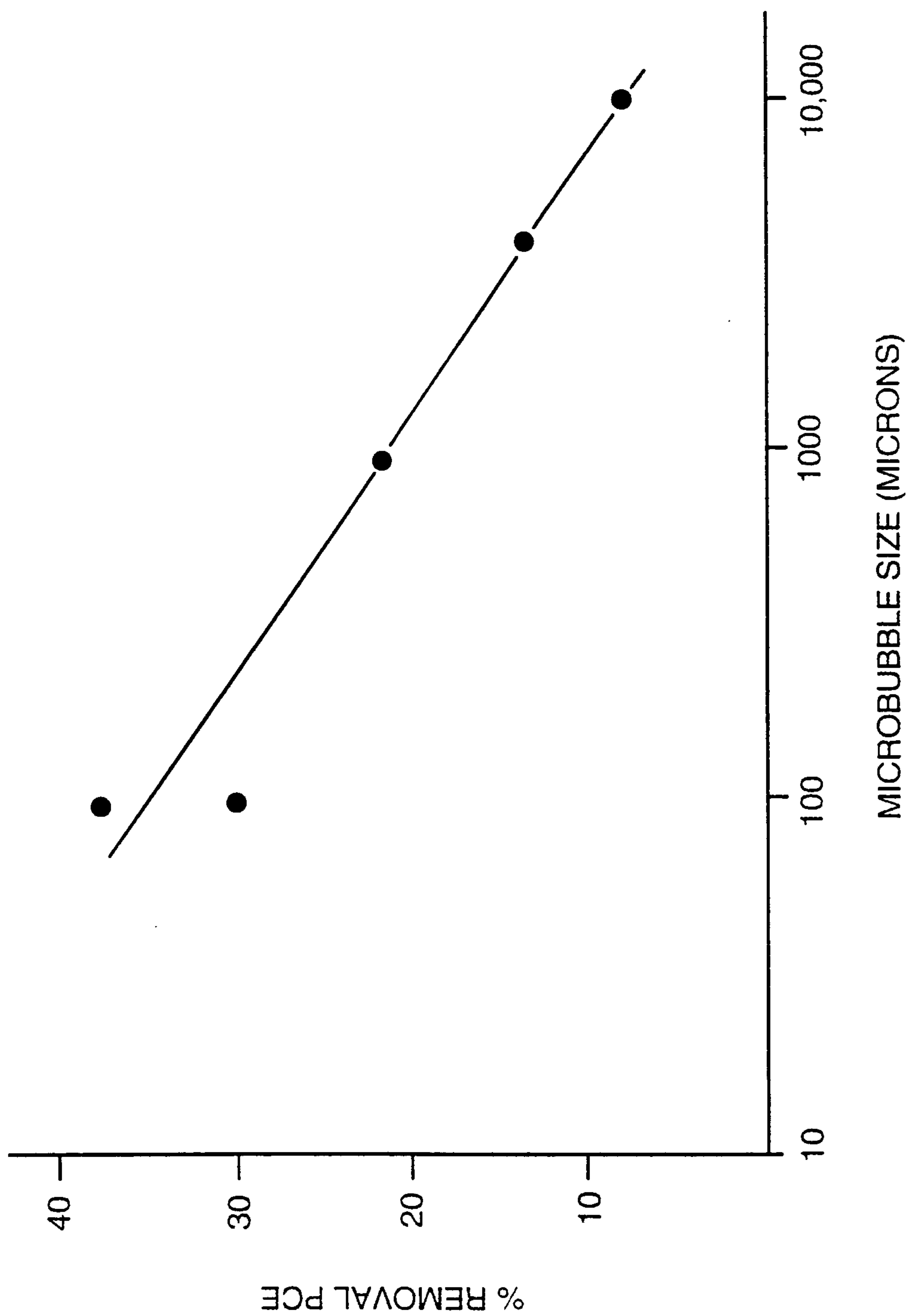


FIG. 10

