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(72) Inventeurs/Inventors:
MANINI, PAOLO, IT;
BOFFITO, CLAUDIO, IT
(73) Propriétaire/Owner:
SAES GETTERS S.P.A., IT
(74) Agent: GOWLING LAFLEUR HENDERSON LLP

(54) Titre : COMBINAISON DE MATERIAUX DE GETTER ET DISPOSITIF CONTENANT LESDITS MATERIAUX
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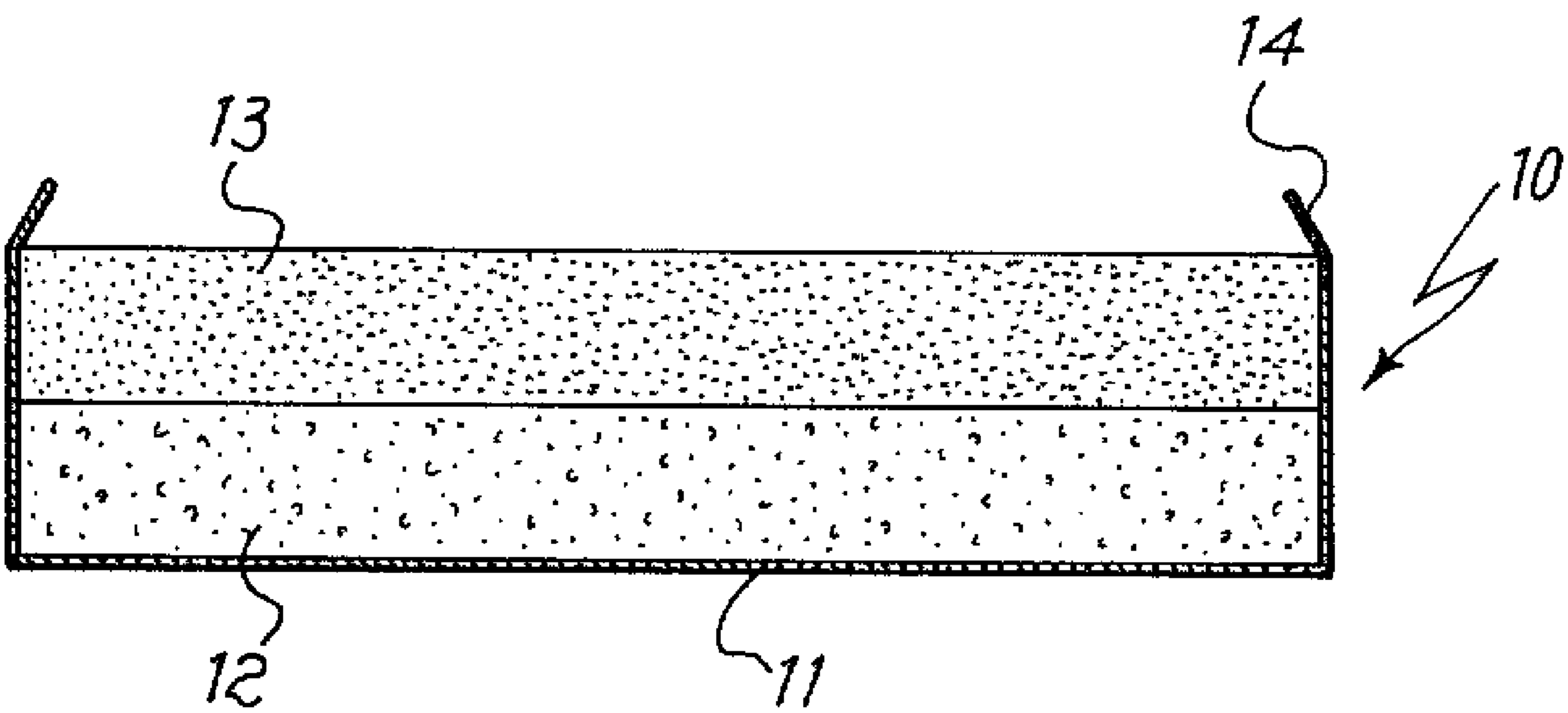

(57) Abrégé/Abstract:
A combination of getter materials particularly suitable to maintain vacuum in devices which cannot be heated at temperatures higher than about 200°C comprises: a) a mixture MO/Pd between an oxide of a transition metal MO chosen among cobalt oxide, copper oxide or their combinations and metallic palladium, wherein the latter is present up to about 2% by weight; and b) a moisture sorbing material. In particular applications it is possible to add to this combination also a barium- and lithium-based alloy, preferably $BaLi_4$. Getter devices for containing such a combination are also described.

"COMBINATION OF GETTER MATERIALS AND DEVICE FOR CONTAINING THE SAME"

ABSTRACT

A combination of getter materials particularly suitable to maintain vacuum in devices which cannot be heated at temperatures higher than about 200°C comprises: a) a mixture MO/Pd between an oxide of a transition metal MO chosen among cobalt oxide, copper oxide or their combinations and metallic palladium, wherein the latter is present up to about 2% by weight; and b) a moisture sorbing material. In particular applications it is possible to add to this combination also a barium- and lithium-based alloy, preferably $BaLi_4$. Getter devices for containing such a combination are also described.

"COMBINATION OF GETTER MATERIALS AND DEVICE FOR CONTAINING THE SAME"

The present invention deals with a new combination of getter materials and the getter devices containing the same. In particular, the present invention relates to a getter combination suitable to the maintenance of vacuum in devices which cannot be heated at temperatures higher than about 200°C.

The getter materials have been found to be practically necessary in all the applications relating to industry and trade which require vacuum to be maintained.

Until few years ago, in all the devices requiring vacuum for their operation, the walls designed to confine the vacuum were made of metal or glass. Evacuated volumes defined by metal walls are present e.g. in the "thermos" or "dewars", in the thermally insulated pipes for the conveyance of cryogenic fluids, or in scientific applications such as the particle accelerators. Evacuated volumes defined by glass walls are instead present e.g. in the cathode-ray tubes for television screens or computer displays and in the lamps. In all these applications the getter material is introduced inactive in the device before its sealing and then activated later, when the device is sealed, by means of heating from the outside, such as with radio-frequency waves. The activated getter adsorbs the last gaseous traces still present in the device and carries out the sorption of those gases which, through various mechanisms, enter the evacuated volume during the life of the device itself. The minimum temperatures required by the conventional getter materials for activation are in the order of 350°-400°C, and in some cases even temperatures of about 900°C can be reached. Getter materials of this type are for example the zirconium- or titanium-based alloys.

However, in the most recent years the use of vacuum in the industrial field has been extended to evacuated devices made, at least in part, of plastic materials, which cannot be heated at temperatures higher than about 200°C; this is for example the case of the thermally insulated jackets under vacuum, wherein the plastic materials can be used to form the walls or the filling materials or both. The filling materials (in the following defined as "fillers") are generally in the form of fibers, powders or foams and are employed in the jackets for maintaining the shape thereof. A typical example of such jackets are evacuated panels, mainly used in the production of refrigerators. The envelope of these panels is generally made of plastic-metal laminated foils, thermally sealed at their edges through a plastic-to-plastic contact; metal-to-metal sealing are avoided in order to break the thermal bridge between the two faces of the panel. The plastic materials cannot be heated at temperatures higher than about 200°C to prevent the chemical and mechanical stability thereof from being jeopardized. Therefore the conventional getter materials are inadequate to this type of use. This has caused the demand for the availability of getter materials with a low temperature of activation or, better, requiring no thermal activation.

The International Patent Application WO 94/18876 discloses the use in combination of an oxide of a noble metal, in particular palladium oxide (PdO), and of a moisture sorbing material, such as barium oxide (BaO), for the maintenance of vacuum in evacuated jackets of dewars, thermos, etc. However the palladium oxide, through a reaction with hydrogen, is converted into metallic Pd in a finely powdered form, having pyrophoric properties; consequently the use of this combination of materials is not recommended for safety reasons.

U.S. Patents 5,312,606 and 5,312,607 in the name of the applicant disclose a family of alloys based on barium and lithium with other elements added such as aluminum or earth-alkaline elements; these alloys are the only known getter materials capable of sorbing practically all gases at room temperature without requiring thermal activation. Specific applications of these materials are described e.g. in the U.S. Patent 5,408,832 and in the International Patent Application WO 96/01966. In particular the preferred alloy is the $BaLi_4$ alloy. In order to ensure the nitrogen sorption capacity of this alloy, which could become exhausted by the sorption of water vapor, the U.S. Patent 5,408,832 discloses the use of $BaLi_4$ in combination with a moisture sorbing material, such as the barium oxide.

Such combination of materials shows very good performances as regards the removal of O_2, N_2 and H_2O, thus eliminating the main atmospherical gases from the gaseous environment at the inside of the jackets. However, the gaseous composition within these jackets mainly depends on the degassing of the materials forming said jackets, in particular the fillers which are generally in the form of powder, foam or wool, and consequently are provided with a great specific surface. The main gases being present in the jackets made of plastic material are CO and CO_2 in case of polymeric filler and H_2 in case of e.g. glass wool. The load of these gases may be important, mainly whenever in the jacket manufacturing process there are heating steps; it is for example the case of the manufacture of refrigerators, wherein the vacuum insulating panels are fixed to the walls of the appliances by means of polymeric foams, generally polyurethanes, obtained by reacting suitable chemical compounds in an *in-situ* foaming process, during which temperatures near to 100°C for times of some minutes may be reached.

Another major contribution to the gas atmosphere inside the panels is from organic compounds, that is, hydrocarbons or susbstitued hydrocarbons in which hydrogen can be replaced partially or completely by halogen atoms. Compounds in which halogen atoms completely replace hydrogen are known as CFCs and have been used for decades in the production of thermal insulating panels for refrigerators. These gases have been recognized as responsible for the ozone-depletion effect, and their production and use have been discontinued. However, it is under study the recycling of old panels containing CFCs through their reduction to powders of the polymeric foams they contain and use of these powders in the production of new panels. Small amounts of CFCs could enter freshly-produced thermal insulating panels by this way. Partially halogen-substituted hydrocarbons, generally referred to as HCFCs, and hydrocarbons have replaced CFCs in this field, and are used as foaming agents both in the production of panels and in the step of fixing the panels to the refrigerator walls by means of foams quite similar to those inside the panels. The most important gases in this application are cyclopentane, C_5H_{10}, and 1,1-dichloro-1-fluoroethane, $Cl_2FC\text{-}CH_3$, this latter known in the technique as 141-b. These latter gases can enter the panels thruogh the edges, in the zone where the plastic-metal laminated foils the envelope is made of are sealed through a plastic-to-plastic thermal sealing: this results in an increasing of the pressure inside the panel and in the worsening of its thermal insulating properties.

The above described combination $BaO/BaLi_4$ can sorb CO, CO_2

and, particularly, H_2, but at a relatively low speed; moreover, prior art getter materials are not known to be able to effectively absorb organic compounds.

It is therefore an object of the present invention to provide a combination of getter materials of improved sorption properties for CO, CO_2 and H_2 and capable to absorb organic compounds, which does not require thermal activation and is therefore compatible with devices in which at least one component cannot be heated at temperatures higher than about 200°C.

Another object of the invention is that of providing a device for using that combination of getter materials.

According to the present invention these and other objects are obtained with a combination of getter materials comprised of:

- a mixture of an oxide of a transition metal chosen among cobalt oxide, copper oxide or their combinations and metallic palladium containing up to about 2% by weight of metallic palladium;

- a moisture sorbing material having a H_2O vapor pressure lower than 1 Pa at room temperature.

Although various cobalt oxides exist, according to the oxidation number of the metal, the only one which is useful for the invention is the oxide having the empirical formula Co_3O_4, wherein the cobalt is present at the same time under the oxidation state II and oxidation state III; in the following of the specification and in the claims with cobalt oxide there will be meant the compound as defined herein. Similarly, with copper oxide in the following of the specification and in the claims the CuO compound will be meant, wherein the copper is present under the state of oxidation II. Furthermore in the following the abbreviation MO will be used for labeling in general one of the two oxides of the transition metals or a combination thereof, and the abbreviation MO/Pd for indicating the mixture between MO and metallic palladium. The properties of these oxides were already known, for instance by an article by Belousov et al., Ukrainskij Chimiceskij Zurnal, 1986, 52, No. 8, but only for the sorption of hydrogen.

During the preparation of the oxide of the transition metal, a precursor of the metallic palladium is added to the latter in such a quantity to have a final mixture containing up to about 2% by weight of the mixture MO/Pd. Palladium can be coprecipitated with the oxide of the transition metal by its introduction into the same mother solution, in the form of soluble salt, e.g. $PdCl_2$; as an alternative palladium may be deposited from a solution onto grains of transition metal oxide being previously formed. The oxide of the transition metal is used in a powdered form with particle size of less than 500 µm, preferably comprised between 1 and 200 µm.

The moisture sorbing material may be chosen among the chemical moisture sorbers; these materials, known in the art, fix the water in an irreversible way through a chemical reaction. Suitable for this application are the chemical dryers having a H_2O vapor pressure lower than 1 Pa at room temperature, as described in US Pat. 5,408,832 to the Applicant. For example the oxides of calcium, strontium, barium and phosphorous or their combinations are considered suitable to the objects of the invention. The use of barium oxide or calcium oxide is particularly preferred. The moisture sorbing material is preferably used in the form of powder having a particle size between about 50 and 500 µm. With a greater particle size an excessive reduction of the surface area of the powder is experienced, whereas with lower particle size there is the risk that, due to the moisture sorption, the powders become excessively compacted, thus rendering difficult the passage of gases through the powders themselves. In order to overcome the problem of compaction of humid powders, it is also possible to add to the moisture sorbing material a powder of an inert material, such as alumina, as described in the mentioned International Patent Application WO 96/01966.

The ratio by weight between the materials of the combination of the invention may vary within broad limits, also depending on the type of use that is foreseen and in particular of the gas mixture to be sorbed. However, in general, the ratio by weight between mixture MO/Pd and the moisture sorbing material can vary between about 5:1 and 1:20, and preferably between 1:1 and 1:5.

In case that in a particular application it is foreseen that the vacuum initially present in the jacket can be subject to degradation also due to the contribution of atmospheric gases such as O_2 and N_2, to the combination MO/Pd with moisture sorber as above described it is possible to add also a barium- and lithium-based alloy among those described in the U.S. Patents 5,312,606 and 5,312,607 mentioned before, which should be referred to for the details about the preparation and properties of these alloys. The barium- and lithium-based alloy is preferably used in a powdered form with particle size of less than about 500 µm, and preferably less than about 150 µm, in order to increase the surface area. The powder may also be slightly compressed as indicated in the cited Application WO 96/01966. The preferred alloy is that of $BaLi_4$ composition, mentioned above.

The barium- and lithium-based alloys and the cobalt or copper oxides have a mutual reaction and should therefore be kept separated in order not to cause alterations of the performances of the getter combination.

The ratios by weight between the barium- and lithium-based alloy and the other components of the combination according to the invention can vary within broad ranges. The ratio by weight between mixture MO/Pd and the barium- and lithium-based alloy may generally vary between 10:1 and 1:5 and preferably between 5:1 and 1:2. The ratio by weight between the moisture sorbing material and the barium- and lithium-based alloy may vary approximately between 50:1 and 1:5, preferably between 20:1 and 1:1.

In a second aspect thereof the invention refers to the getter devices containing the combination of materials so far described. In the following description reference is made to the drawings in which:

FIGURE 1 shows a possible embodiment of a getter device of the invention; FIGURE 1. a shows a possible alternative embodiment of a getter device of the invention;

FIGURE 2 shows a possible embodiment of the getter device of the invention in case of a mixture with three components MO/Pd, moisture sorbing material and barium- and lithium-based alloy;

FIGURE 3 shows the preferred embodiment of the getter device according to the invention in the case of a mixture with three components MO/Pd, moisture sorbing material and barium- and lithium-based alloy;

FIGURE 4 shows a graph relating to the sorption of a mixture of gases by a getter device containing a combination of materials of the invention, as compared to the sorption of the same mixture of gases by a getter device of the prior art;

FIGURE 5 shows a graph relating to the sorption of a mixture of gases by a getter device containing a combination of materials of the invention including the optional barium- and lithium-based alloy;

FIGURE 6 shows the comparison between the sorption of carbon dioxide (CO_2) by a getter device containing a combination of materials of the invention including the optional barium- and lithium-based alloy and by a prior art getter device;

FIGURE 7 shows a graph relating to the sorption of cyclopentane by a getter device containing a combination of materials of the invention;

FIGURE 8 shows a graph relating to the sorption of a HCFC gas by a getter device containing a combination of materials of the invention;

FIGURE 9 shows a graph relating to the sorption of a CFC gas by a getter device containing a combination of materials of the invention;

FIGURE 10 shows a graph relating to the sorption of nitrogen by a getter device containing a combination of materials of the invention, including the optional barium- and lithium-based alloy, after absorption of cyclopentane.

The combination of getter materials according to the invention is preferably used by placing it within a container, in order to have a compact getter device, easy to handle. The container is preferably made of a material which is impermeable to gases and has an opening of such a size that the gases have access to the various getter materials according to a given order. This because it has been found that the water vapor impairs the properties of the mixture MO/Pd.

The container is generally made of metals, that are impermeable to gases. Preferred metals are aluminum, which has light weight and is easy to be machined at low cost; and stainless steel, when higher mechanical strength is desired, mainly for automated handling of getter devices.

A possible embodiment is illustrated in Fig. 1, where a getter device 10 according to the invention is shown being formed of a holder 11 made of aluminum, the lower portion of which contains a layer of MO/Pd mixture 12, and the upper portion a layer of powder of a moisture sorbing material 13. These materials may be introduced in the holder in various ways, for example by pouring the powder into the holder and subjecting it to a slight compression, or by introducing into the holder some pre-formed pellets. In both cases it is also possible that at the interface between the layers of different materials there are elements of mechanical separation which allow an easy passage of gases, such as nets of plastic material, gauzes, disks of porous paper (not shown in the figure). These elements help to keep the materials separated from each other and to hold fragments of material that may be produced in consequence of impacts or e.g. by swelling of the powders due to the gas sorption. Finally the upper edge of the holder 11 is slightly bent inwards, thus forming a retention element 14 which keeps the getter structure in the desired position.

In another possible embodiment, the upper edge of the holder is not bent inwardly. This embodiment is preferred when the getter device is intended for use in applications where the filler is a polymeric foam, e.g. polyurethane. In this case a straight upper edge performs a cutting action, and it makes easier the insertion of the device in the foam panel by compression, mainly in automated productions. This embodiment is shown at Fig. 1.a, where the elements making up the device are referred to by the same numbers as in Fig. 1, but for element number 15 that is the non-bent upper edge.

In case that the ternary combination of materials is used, comprising also a barium- and lithium-based alloy, in manufacturing the device it should be considered that these alloys can react with the mixture MO/Pd, and thereby these two materials have to be kept separated; furthermore, like the mixture MO/Pd, also the barium- and lithium-based alloys are sensible to water, whereby they should be protected therefrom. To carry out these conditions, various constructions of the getter devices are possible. In the simplest embodiment, as shown in Fig. 2, a device 20 is used, composed of a holder 21 including at the inside, when going from the bottom upwards, a layer 22 of mixture MO/Pd, a layer 23 of moisture sorptive material, a layer 24 of a barium- and lithium-based alloy and finally, in contact with the external environment, a second layer 25 of moisture sorptive material. Like in the device of Fig. 1, the upper edge of the holder 21 may be inwardly bent thus defining a retention element 26 which keeps the layers of various materials at the desired position. In alternative, the upper edge of the holder may be of the non-bent kind, as in Fig. 1.a (not shown). The layers of material from 22 to 25 can be either introduced in the form of loose powders to the holder 21 where they can be possibly subjected to a light pressure to enhance the mechanical stability of the layer, or pellets of the materials may be prepared separately for their subsequent introduction into the container 21. In both cases it is possible to separate the different layers by means of elements of mechanical separation such as polymeric gauzes or the like, not shown in the drawing, such as described in case of the device of Fig. 1.

A preferred embodiment of the getter device containing also the barium- and lithium-based alloy is shown in Fig. 3. In this case the getter device 30 is composed of a first holder 31 made of stainless steel or aluminum, containing on its bottom a layer or a pellet 33 of powdered mixture MO/Pd; a second holder 32 made of stainless steel is placed over the layer 33 and filled with barium- and lithium-based alloy 34. The assembly formed of the powdered mixture MO/Pd 33, holder 32 and the powdered barium- and lithium-based alloy 34 is then coated with powder of a moisture sorptive material 35. On the upper portion of the powder 35, exposed to the outside, an element of mechanical retention is preferably placed to allow an easy passage of gases, such as a polymeric net or a gauze 36. Like in the structure of Fig. 1, such polymeric gauzes may be also positioned over the layer of MO/Pd and over the powder of barium- and lithium-based alloy to prevent the powders from mixing up and to enhance the mechanical stability of the resulting structure (these additional polymeric gauzes are not shown in the drawing). Finally, the upper edge of the holder may be slightly bent to the inside thus forming a retention element 37 to keep the resulting getter structure at its position, or may be of the non-bent kind to help introduction of the device in polymeric foam panels, as shown in Fig 1.a (this last possibility not shown in the drawings).

Objects and advantages of the present invention will result more clearly apparent to those skilled in the art from the following examples, which have a merely explanatory purpose and thereby do not limit the scope of the invention.

EXAMPLE 1

This example refers to the preparation of a getter device according to the invention.

1 g of mixture Co_3O_4/Pd, including 10 mg of Pd, is placed on the bottom of a cylindrical holder of stainless steel having a diameter of 28 mm and height of 4 mm and is lightly pressed; over the layer of Co_3O_4/Pd thus obtained a gauze of a polymeric material is positioned to keep the powder at the desired position. 4.5 g of BaO are introduced in the holder, over this

first layer, and are then pressed lightly. The upper edge of the holder is finally deformed by bending to the inside in such a way to hold both layers in their starting configuration, thus obtaining a device corresponding to the one shown in Fig. 1.

EXAMPLE 2

This example refers to the preparation of a second getter device of the invention comprising, in addition to the mixture MO/Pd and the moisture sorbing material, also a barium- and lithium-based alloy.

1 g of mixture Co_3O_4/Pd, containing 10 mg of Pd, is placed on the bottom of a first cylindric holder of stainless steel having a diameter of 28 mm and height of 6 mm and is lightly pressed; over the obtained layer of Co_3O_4/Pd a gauze of polymeric material is positioned to keep the powder at a desired position. A second cylindric holder of steel, having a diameter of 15 mm and height of 3 mm, is prepared separately and is filled with 0.25 g of $BaLi_4$ alloy, lightly compressed and coated with a gauze of polymeric material. The holder of $BaLi_4$ alloy is introduced in the first holder, over the gauze that keeps in position the mixture Co_3O_4/Pd. 4 g of powdered BaO are then poured into the first holder until completely coating both the Co_3O_4/Pd mixture and the holder with $BaLi_4$ alloy. The powdered BaO is made level, lightly compressed and covered by means of a gauze of a polymeric material to keep it in position. Finally, the upper edge of the first holder is slightly bent inwardly to keep in position the whole structure, thus obtaining a getter device corresponding to that shown in Fig. 3.

EXAMPLE 3

This example deals with the test of gas sorption by the getter device of Example 1.

The device according to the Example 1 is placed in a measuring chamber having a volume of 1,5 l which is connected to a capacity pressure gauge and, through intercepting valves, to inlet and outlet gas pipings. A gaseous mixture is introduced in the measuring chamber which comprises 50% CO and 50% H_2, as a simulation of a possible gaseous environment in a plastic jacket containing a filler, until reaching a total pressure in the chamber of 0.32 mbar. Finally the chamber is closed and the pressure variations (mbar) are monitored in function of the time (minutes). The result of the test, that is carried out at room temperature, is

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plotted in Fig. 4 as curve 1.

EXAMPLE 4 (COMPARATIVE)

The test of example 3 is repeated, but using a getter device of the prior art in place of a getter device of the invention. The comparison getter device has a structure similar to that of example 1, but containing 0.25 g of $BaLi_4$ and 4.5 g of BaO. The result of this test is plotted in Fig. 4 as curve 2.

EXAMPLE 5

This example deals with the test of gas sorption by the getter device of Example 2.

The test of Example 3 is repeated, except for introducing in the measuring chamber a gaseous mixture comprising 33.3% CO, 33.3% H_2 and 33.3% N_2. The variations of the pressure in the chamber are monitored in function of the time at the presence of the device of Example 2. The test result is plotted in Fig. 5 as curve 3, giving the overall pressure in the chamber (mbar) as a function of time (minutes).

EXAMPLE 6

This example deals with the test of gas sorption by a getter device similar to that of example 1, where BaO is replaced by CaO.

A getter device containing 2 g of CaO, 1 g of Co_3O_4 and 10 mg of Pd is introduced in a measuring chamber similar to that of example 3, of total volume 0.74 l. The chamber is evacuated at a pressure of $1.33 \cdot 10^{-5}$ mbar. CO_2 is then let in the chamber until reaching a pressure of 0.86 mbar, and the pressure variations (mbar) are monitored as a function of time (minutes). The result of this test is plotted in Figure 6 as curve 4.

EXAMPLE 7 (COMPARATIVE)

The test of example 6 is repeated, but using the prior art getter device of example 4. The result of this test is plotted in Fig. 6 as curve 5.

EXAMPLE 8

This example deals with the test of gas sorption by the getter device of Example 2.

The test of Example 3 is repeated, except for introducing in the measuring chamber cyclopentane as the test gas. The variations of the pressure in the chamber are monitored in function of the time at the presence of the device of Example 2. The test result is plotted in a semilogarithmic graph in Fig. 7 as curve 6, as pressure (mbar) as a function of time (minutes).

EXAMPLE 9

This example deals with the test of gas sorption by the getter device of Example 1.

The test of Example 3 is repeated, except for introducing in the measuring chamber 141-b gas. The variations of the pressure in the chamber are monitored in function of the time at the presence of the device of Example 1. The test result is plotted in a semilogarithmic graph in Fig. 8 as curve 7, as pressure (mbar) as a function of time (minutes).

EXAMPLE 10

This example deals with the test of gas sorption by the getter device of Example 1.

The test of Example 3 is repeated, except for introducing in the measuring chamber the CFC gas known as CFC 11. The variations of the pressure in the chamber are monitored in function of the time at the presence of the device of Example 1. The test result is plotted in a semilogaritmic graph in Fig. 9 as curve 8, as pressure (mbar) as a function of time (minutes)..

EXAMPLE 11

This example deals with the test of gas sorption by the getter device of Example 2.

After completion of example 8, nitrogen is let in the chamber until a pressure of about 1.45 mbar is reached. The chamber is closed and the pressure variations (mbar) are monitored as a function of time (minutes). The result of this test is plotted in Figure 10 as curve 9.

Examining the results of examples 3 to 10 it is clearly seen that the combination of materials of the invention effectively absorbs all the gases that are expected to enter thermal insulating jackets, and particularly panels for refrigerators, during their operation. In particular, it is seen that gases such as hydrogen and carbon monoxide are absorbed in a few minutes, where prior art getters of low activation temperature required longer times; also, it is seen that the combinations of the invention are unexpectedly able to sorb organic gases, ranging from hydrocarbons to wholly halogen-substituted hydrocarbons, CFCs, through intermediate HCFCs; finally, the results of tests show that the sorption of nitrogen, representative of atmospheric gases, is not impaired by previous (or, in operation, simultaneous) absorption of organic gases. The combinations of materials of the invention and the devices containing them represent thus a reliable solution to the problem of keeping the desired degree of vacuum inside thermal insulting jacket that cannot whitstand thermal treatment above 150°C and that work at room temperature.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A combination of getter materials consisting of:
a mixture MO/Pd of an oxide of a transition metal MO chosen among Co_3O_4, CuO or their combinations and metallic palladium containing up to about 2% by weight of metallic palladium ,wherein the MO/Pd mixture is used in the form of powder with a particle size of less than 500 μm; and
a moisture sorbing material having a H_2O vapor pressure lower than 1 Pa at room temperature.

2. A combination of getter materials according to claim 1, in which the MO/Pd mixture is used in the form of powder with particle size between 1 and 200 μm.

3. A combination of getter materials according to claim 1, in which the moisture sorbing material is chosen among the oxides of calcium, strontium, barium and phosphorous or their combinations.

4. A combination of getter materials according to claim 3, in which the moisture sorbing material has a particle size comprised between about 50 and 500 μm.

5. A combination getter materials according to claim 3, in which powdered alumina is added to the moisture sorbing material.

6. A combination of getter materials according to claim 3, in which the moisture sorbing material is barium oxide.

7. A combination of getter materials according to claim 3, in which the moisture sorbing material is calcium oxide.

8. A combination of getter materials according to claim 1, in which the ratio by weight between MO/Pd mixture and the moisture sorbing material can vary between about 5:1 and 1:20.

9. A combination of getter materials according to claim 8, in which the weight ratio between the MO/Pd mixture and the moisture sorbing material can vary between 1:1 and 1:5.

10. A combination of getter materials according to claim 1, further containing a barium- and lithium-based alloy.

11. A combination of getter materials according to claim 10, in which the barium- and lithium-based alloy has a particle size of less than about 500 μm.

12. A combination of getter materials according to claim 11, in which the barium- and lithium-based alloy has a particle size of less than 150 μm.

13. A combination of getter materials according to claim 10, in which the barium- and lithium-based alloy is $BaLi_4$.

14. A combination of getter materials according to claim 10, in which the weight ratio between MO/Pd mixture and the barium- and lithium-based alloy can vary between about 10:1 and 1:5.

15. A combination of getter materials according to claim 14, in which the weight ratio between the MO/Pd mixture and the barium- and lithium-based alloy can vary between about 5:1 and 1:2.

16. A combination of getter materials according to claim 10, in which the weight ratio between the moisture sorbing material and the barium- and lithium-alloy can vary between about 50:1 and 1:5.

17. A combination of getter materials according to claim 16, in which the weight ratio between the moisture sorbing material and the barium- and lithium-alloy can vary between about 20:1 and 1:1.

18. A getter device comprising an upwardly open holder made of a gas impermeable material, comprising when going from the bottom of the holder up to the open end of the holder:

a MO/Pd mixture between an oxide of a transition metal MO chosen among Co_3O_4, CuO or their combinations and metallic palladium, comprising up to about 2% by weight of metallic palladium, wherein the MO/Pd mixture is used in the form of powder with a particle size of less than 500 μm; and

a moisture sorbing material having a H_2O vapor pressure lower than 1 Pa at room temperature; wherein only the moisture sorbing material is directly in contact with the external environment.

19. A getter device according to claim 18, in which an upper edge of the holder is bent inwardly.

20. A getter device according to claim 18, in which an upper edge of the holder is not bent inwardly.

21. A getter device according to claim 18, wherein the holder is made of a metal chosen between stainless steel and aluminum.

22. A getter device according to claim 18, wherein the two different getter materials are separated by members of mechanical separation which allow gases to easily flow therethrough.

23. A getter device comprising an upwardly open holder made of a gas impermeable material, comprising when going from the bottom of the holder up to the open end of the holder:

a MO/Pd mixture between an oxide of a transition metal MO chosen among Co_3O_4, CuO or their combinations and metallic palladium, including up to about 2% by weight of metallic palladium, wherein the MO/Pd mixture is used in the form of powder with a particle size of less than 500 μm;

a barium- and lithium-based alloy; and

a moisture sorbing material having a H_2O vapor pressure lower than 1 Pa at room temperature; wherein only the moisture sorbing material is directly in contact with the external environment.

24. A getter device according to claim 23 further comprising a second layer of moisture sorbing material.

25. A getter device according to claim 24, in which an upper edge of the holder is bent inwardly.

26. A getter device according to claim 24, in which an upper edge of the holder is not bent inwardly.

27. A getter device according to claim 23, consisting of:

a first holder being upwardly open and made of a gas impermeable material;

a layer of MO/Pd mixture placed on the bottom of the first holder;

a second holder being upwardly open and positioned over the layer of MO/Pd mixture such that the height of the second holder added to the height of the layer of MO/Pd mixture is less than the height of the first holder being measured at its inner side;

a barium- and lithium-based alloy within the second holder; and

a moisture sorbing material within the first holder so as to completely cover the second holder and the layer of MO/Pd mixture.

28. A device according to claim 27, wherein an upper edge of the first holder is bent inwardly.

29. A device according to claim 27, wherein an upper edge of the first holder is not bent inwardly.

30. A getter device according to claim 27, wherein the first holder is made of aluminum and the second holder is made of stainless steel.

31. A getter device according to claim 27, wherein over the layer of moisture sorbing material there is placed a member of mechanical retention.

32. A thermally insulating jacket made at least partially of plastic material containing a combination of getter materials comprising:

a MO/Pd mixture between an oxide of a transition metal MO chosen among Co_3O_4, CuO or their combinations and metallic palladium, including up to about 2% by weight of metallic palladium, wherein the MO/Pd mixture is used in the form of powder with a particle size of less than 500 μm; and

a moisture sorbing material having a H_2O vapor pressure lower than 1 Pa at room temperature.

33. A thermally insulating jacket made at least partially of plastic material containing a combination of getter materials comprising:

a MO/Pd mixture between an oxide of a transition metal MO chosen among Co_3O_4, CuO or their combinations and metallic palladium including up to about 2%

by weight of metallic palladium, wherein the MO/Pd mixture is used in the form of powder with a particle size of less than 500 μm;

a moisture sorbing material having a H_2O vapor pressure lower than 1 Pa at room temperature; and

a barium- and lithium-based alloy.

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Fig. 1

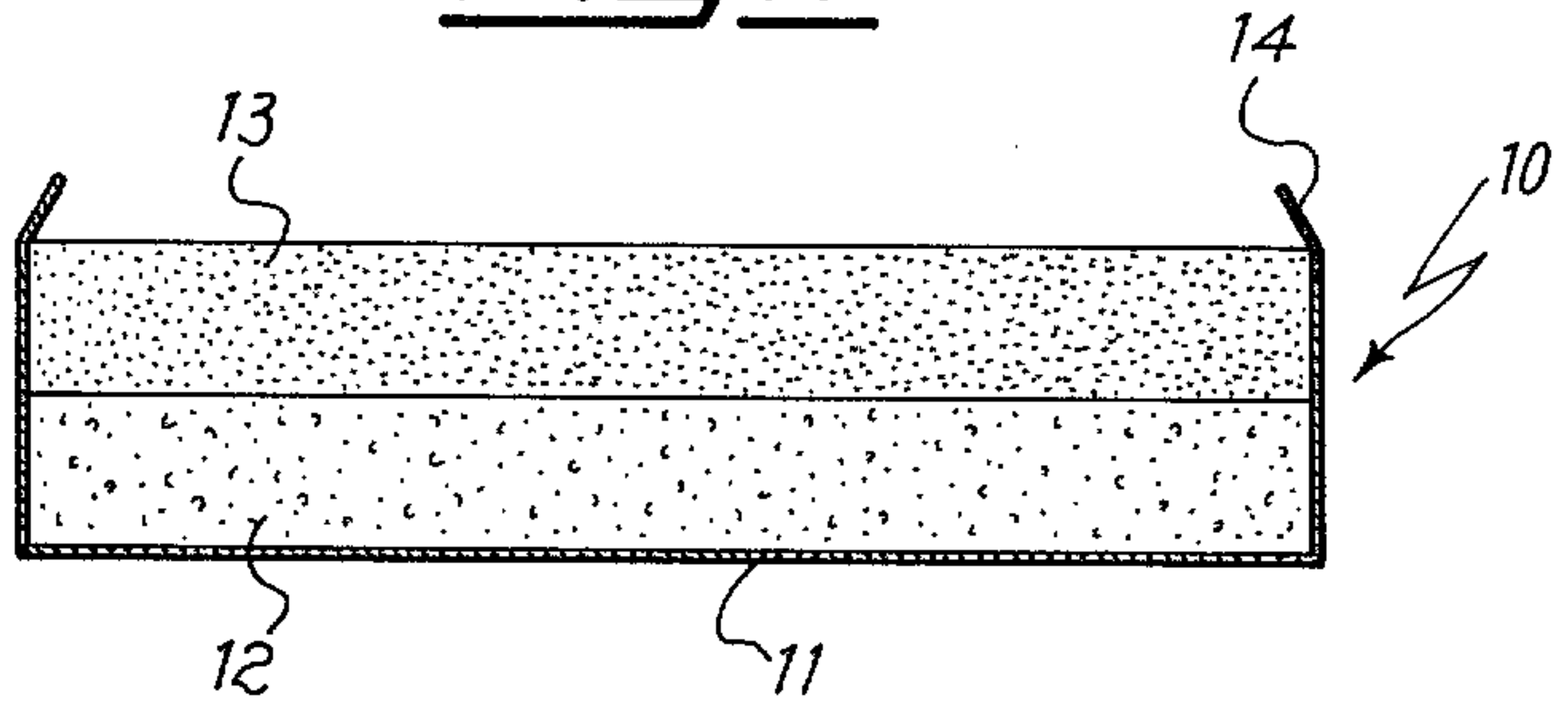


Fig. 2

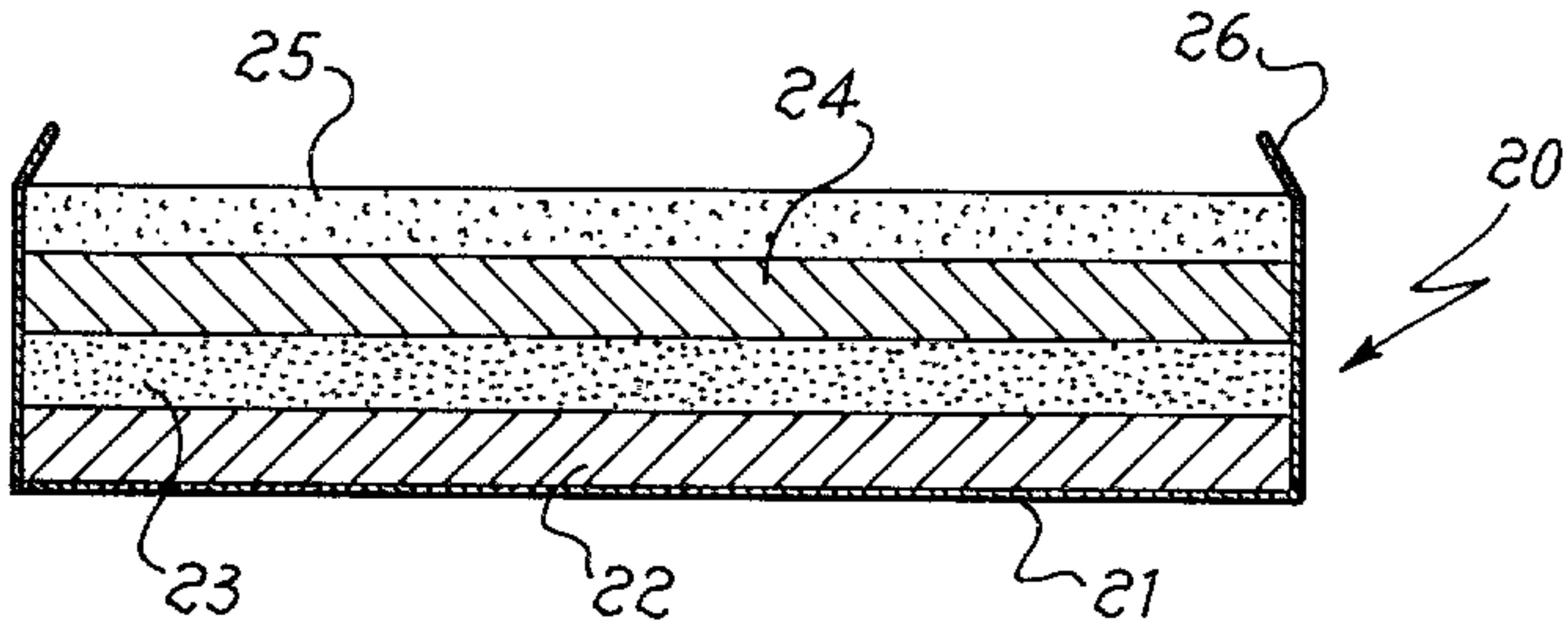
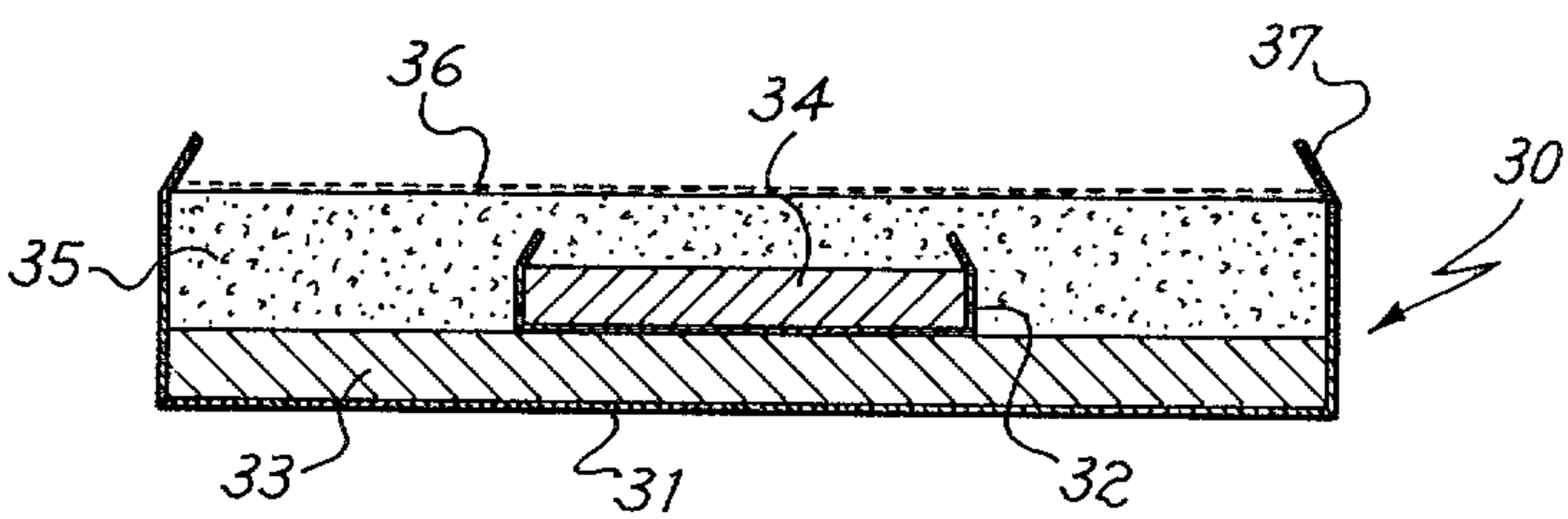


Fig. 3



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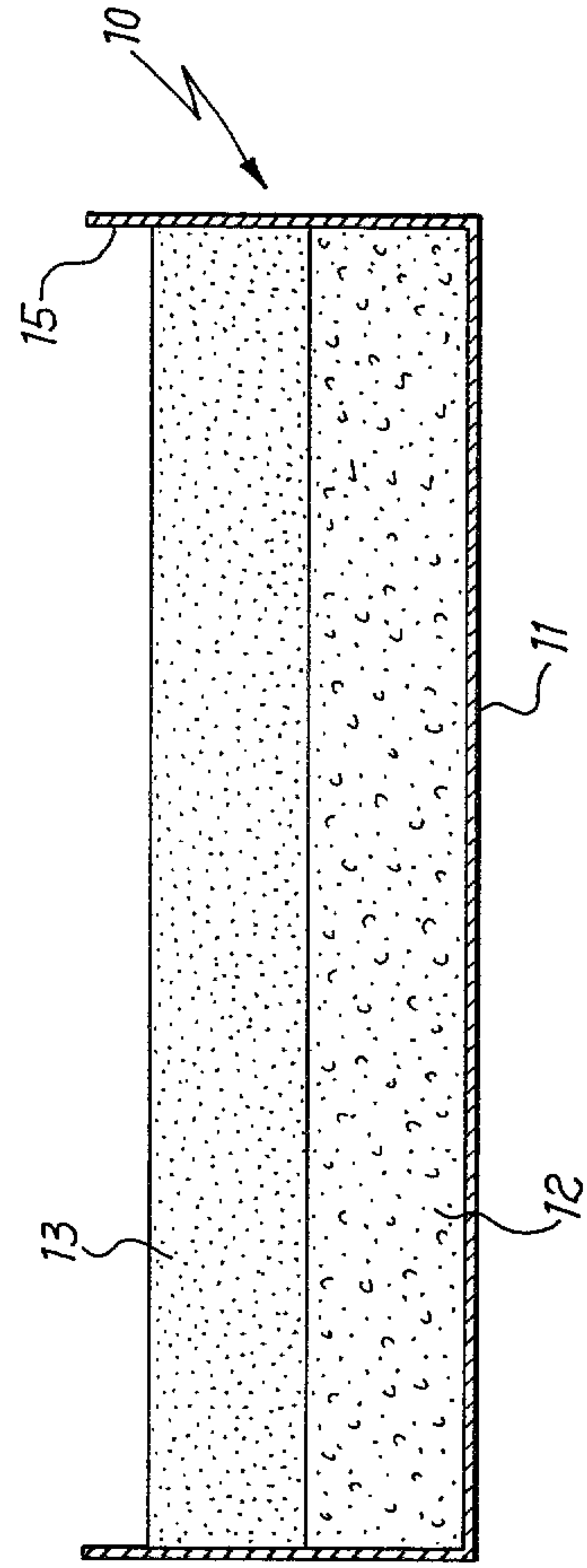

Fig.1a

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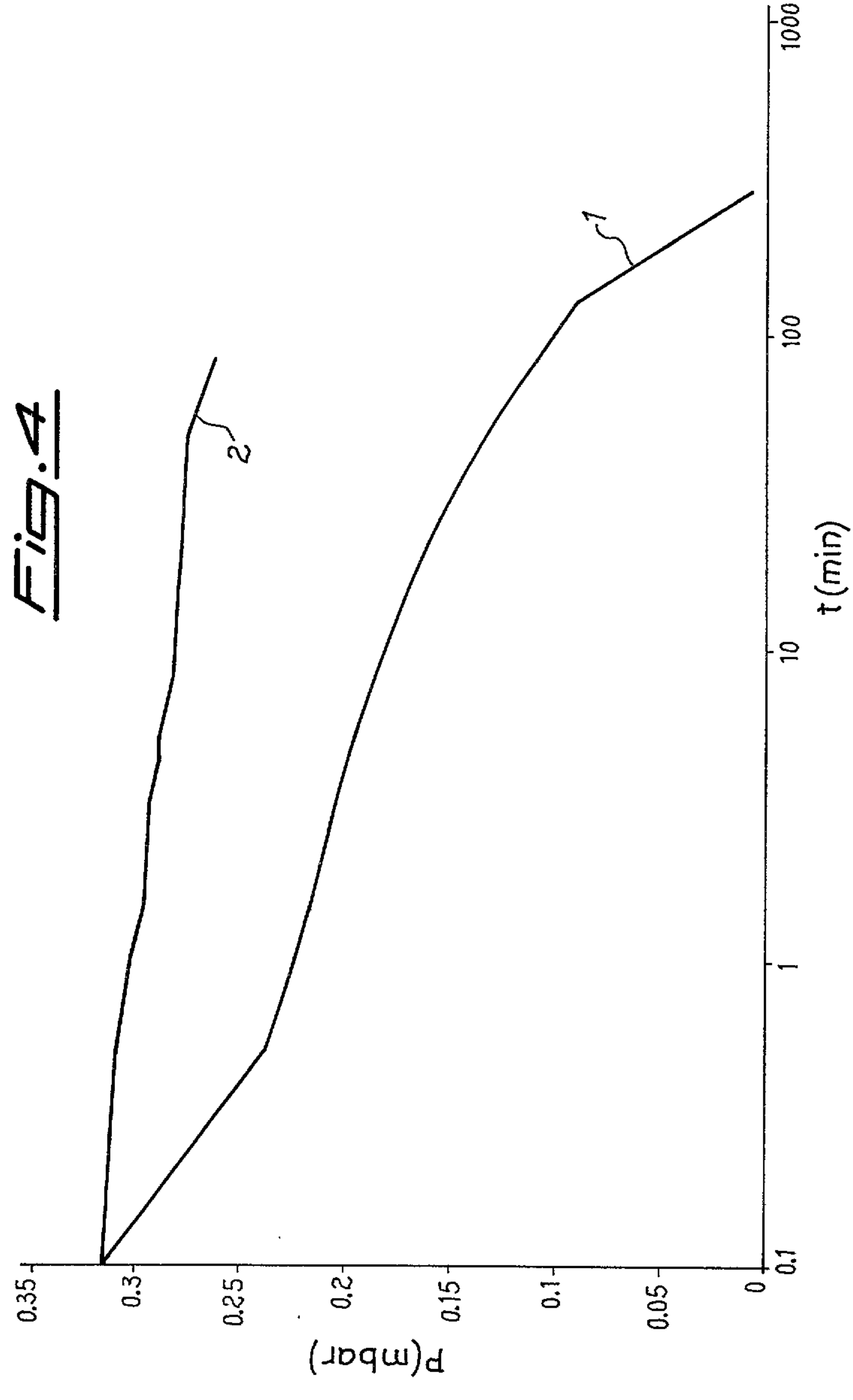

Fig.4

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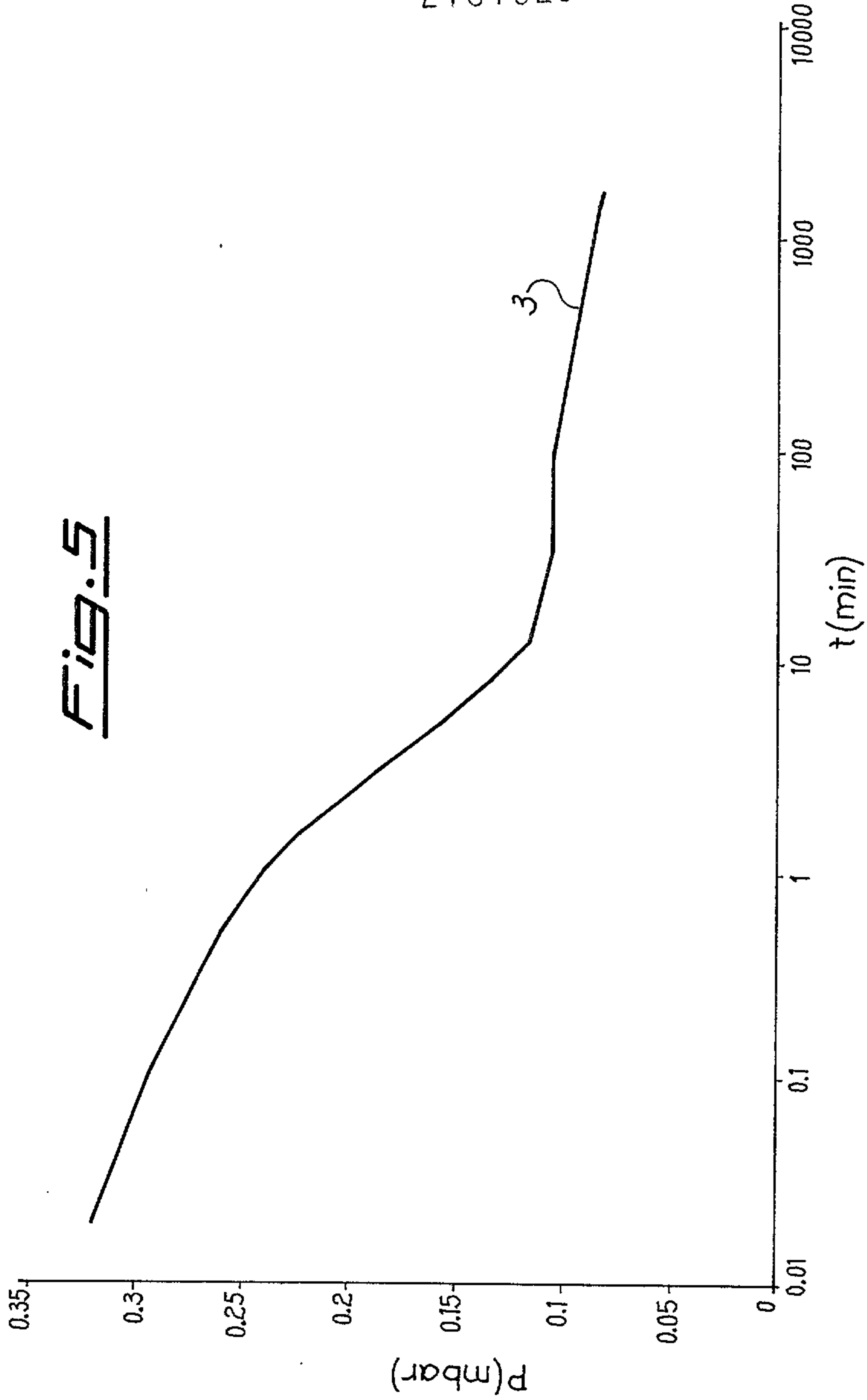

Fig. 5

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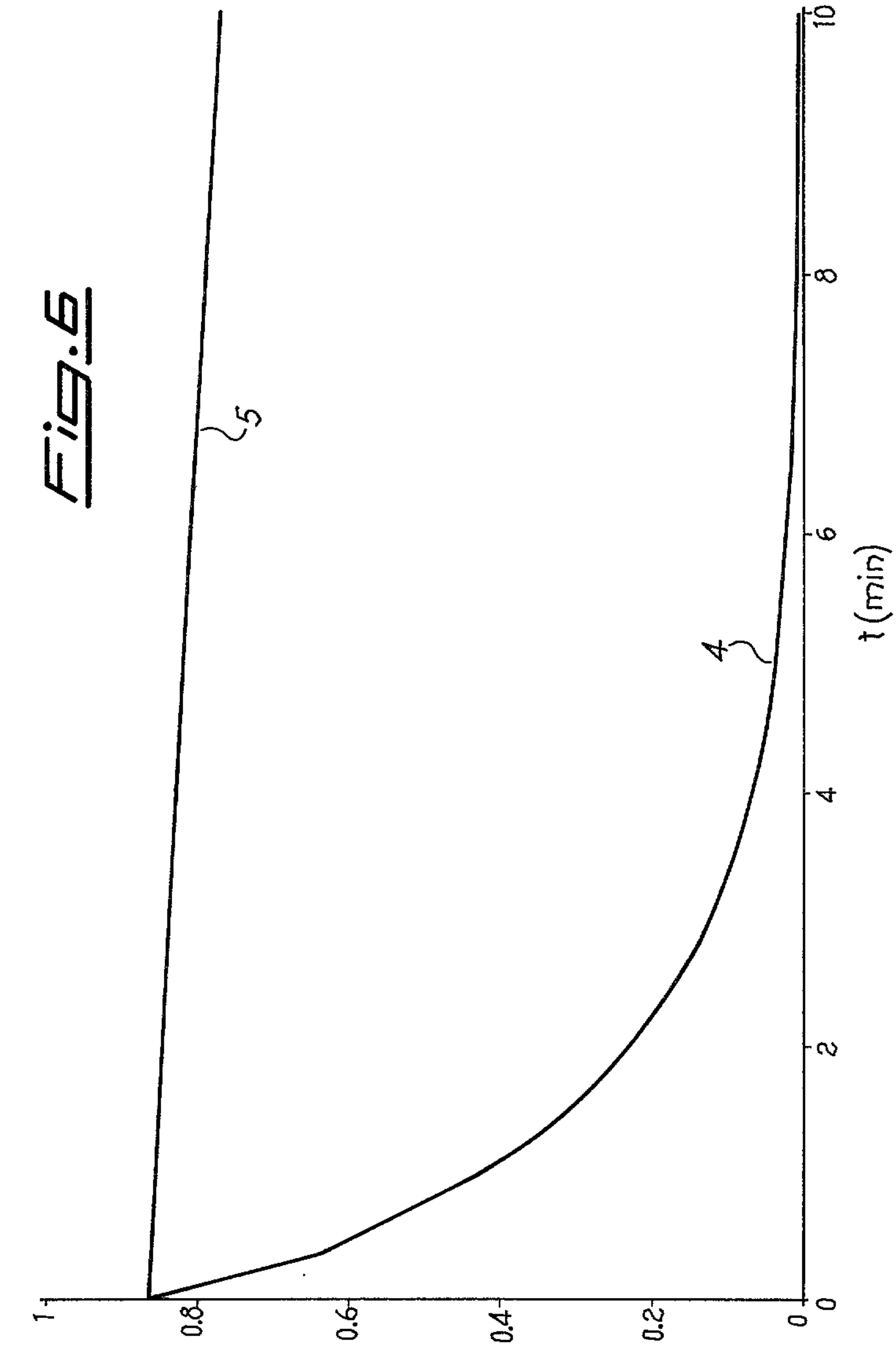

Fig.6

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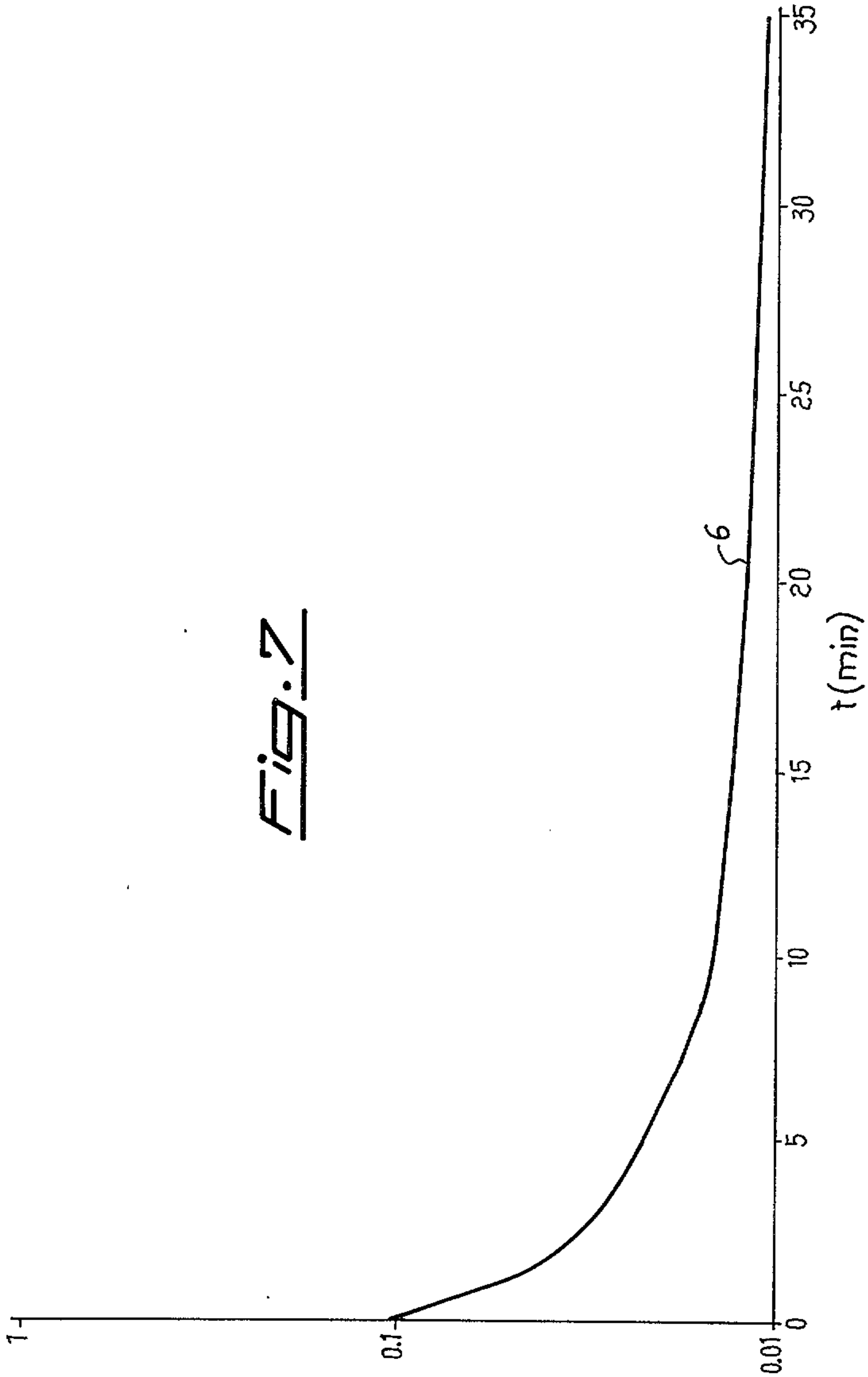

Fig.7

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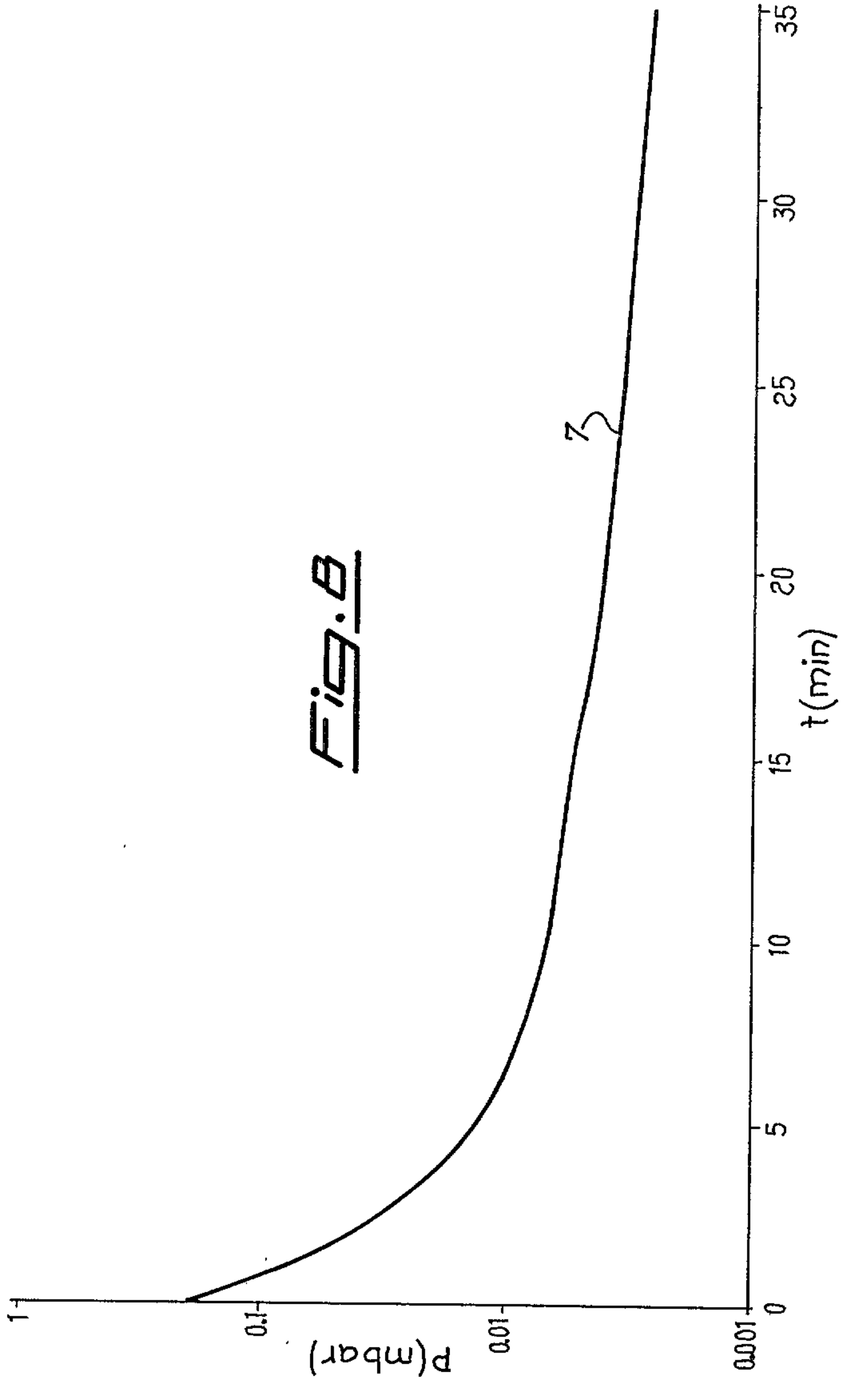

Fig.8

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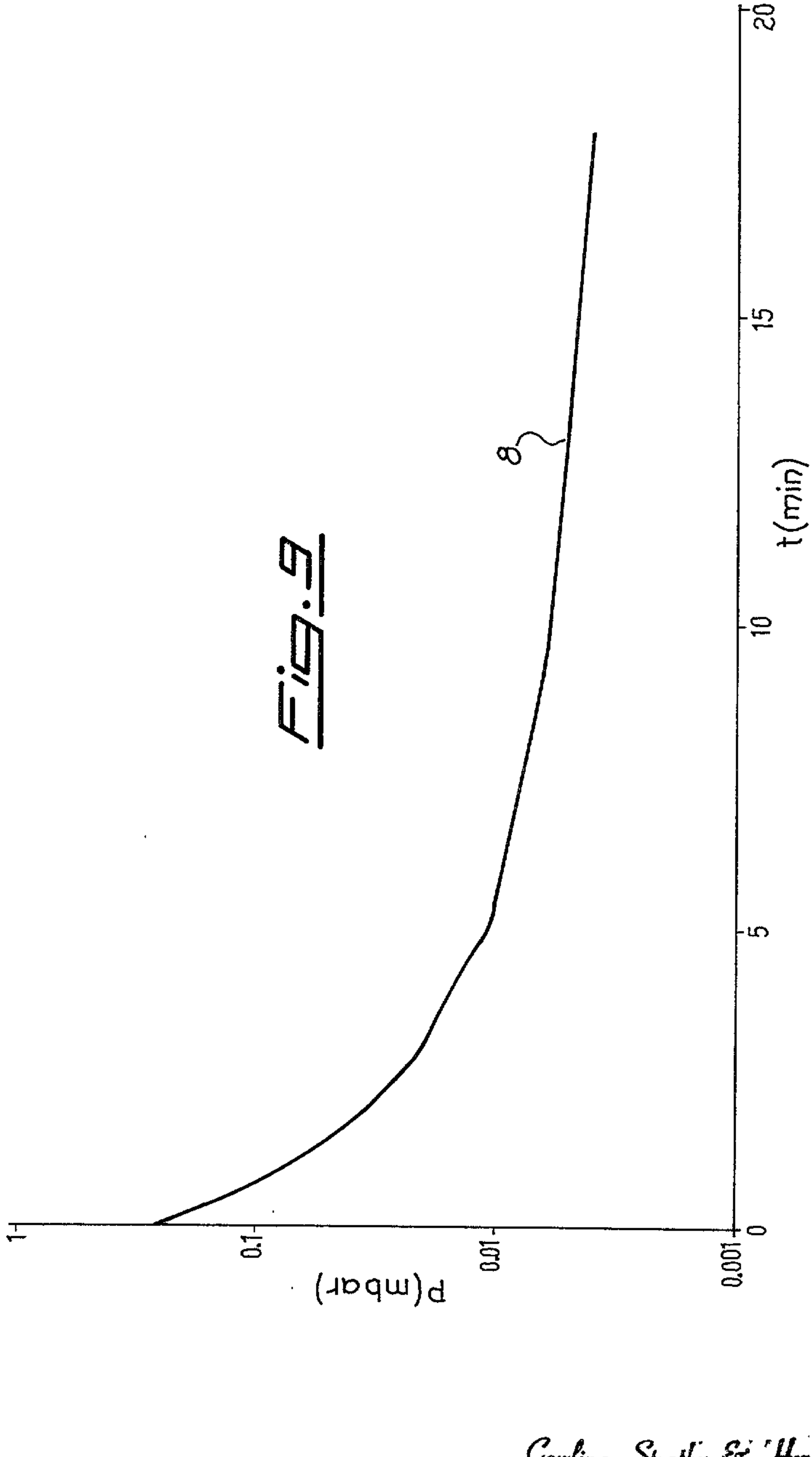

Fig. 9

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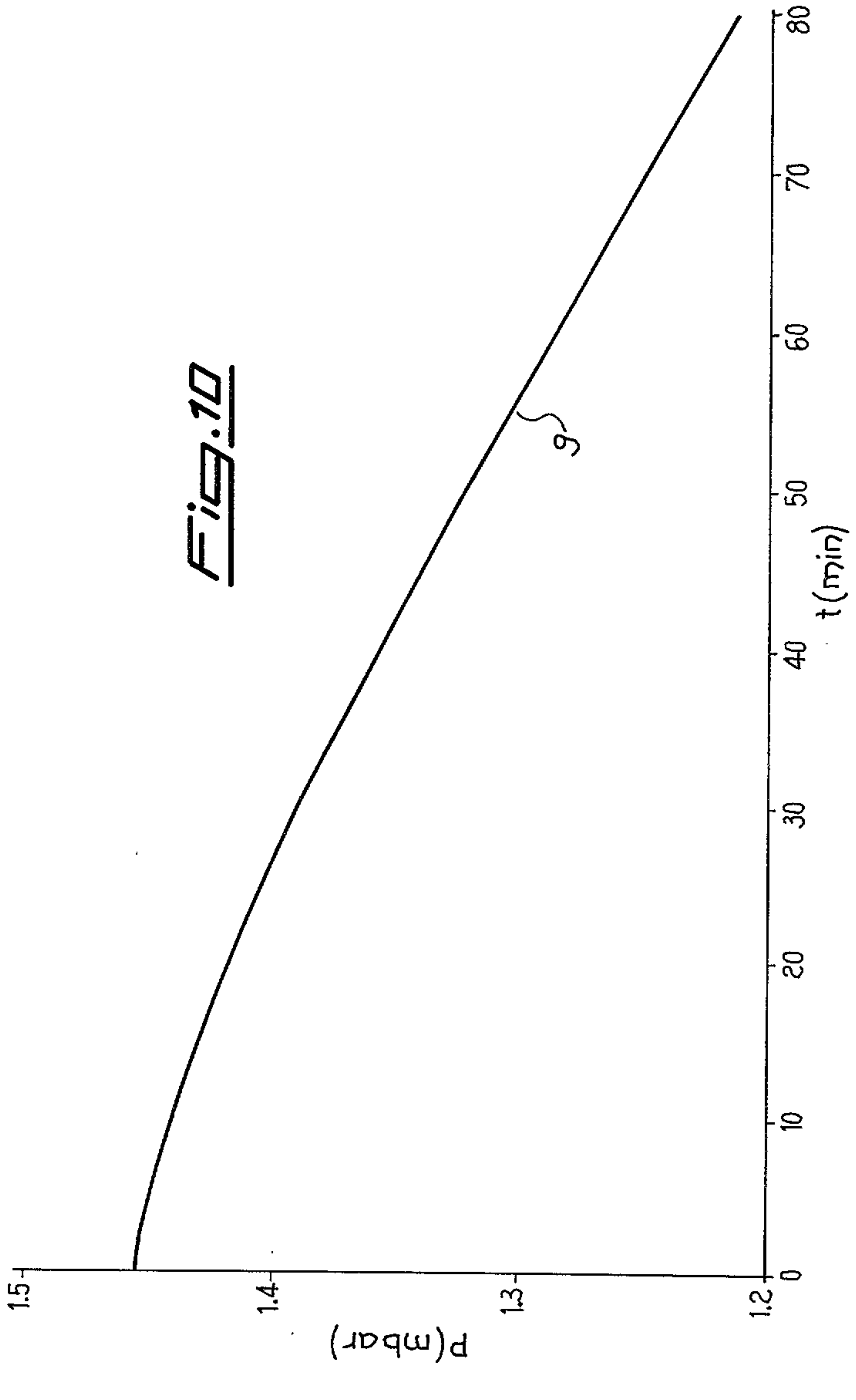

Fig.10

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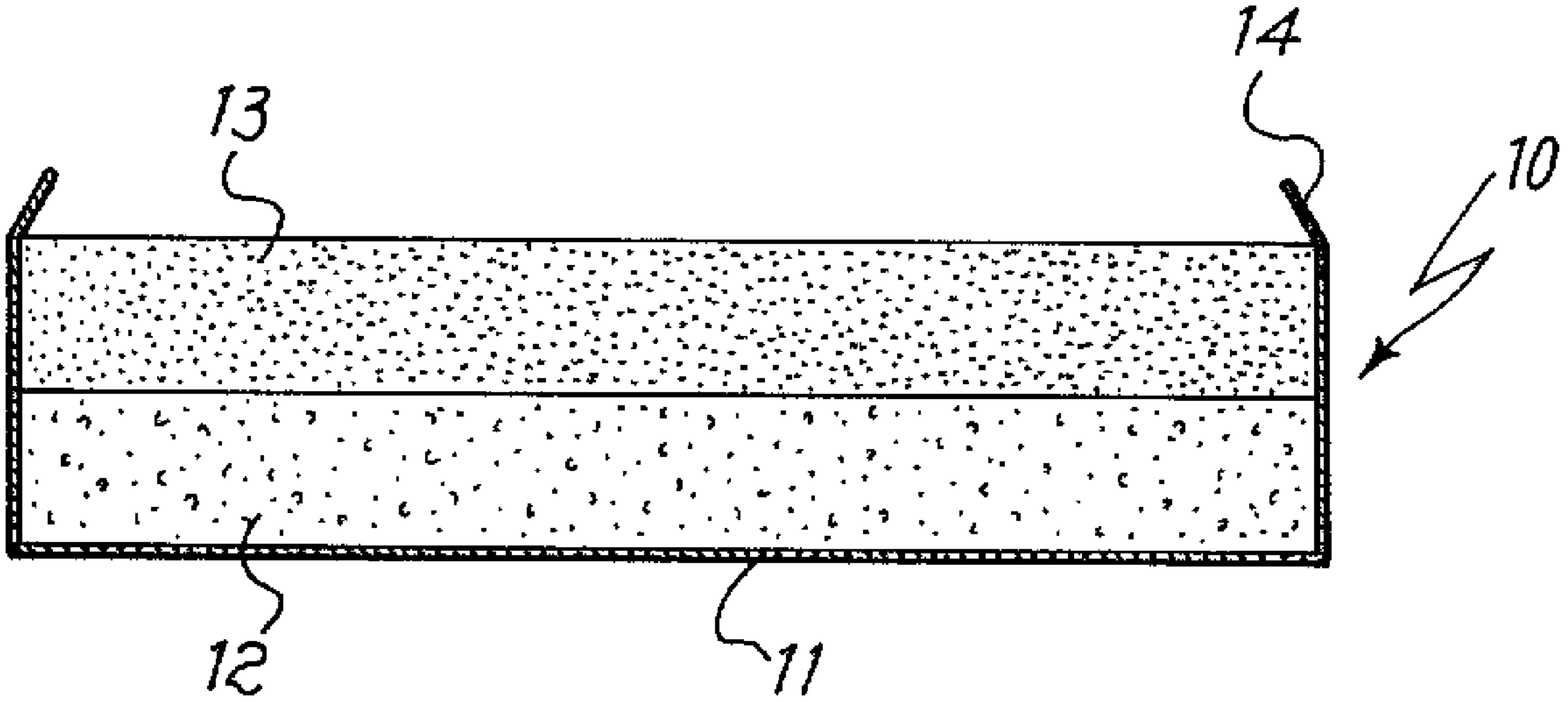
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