

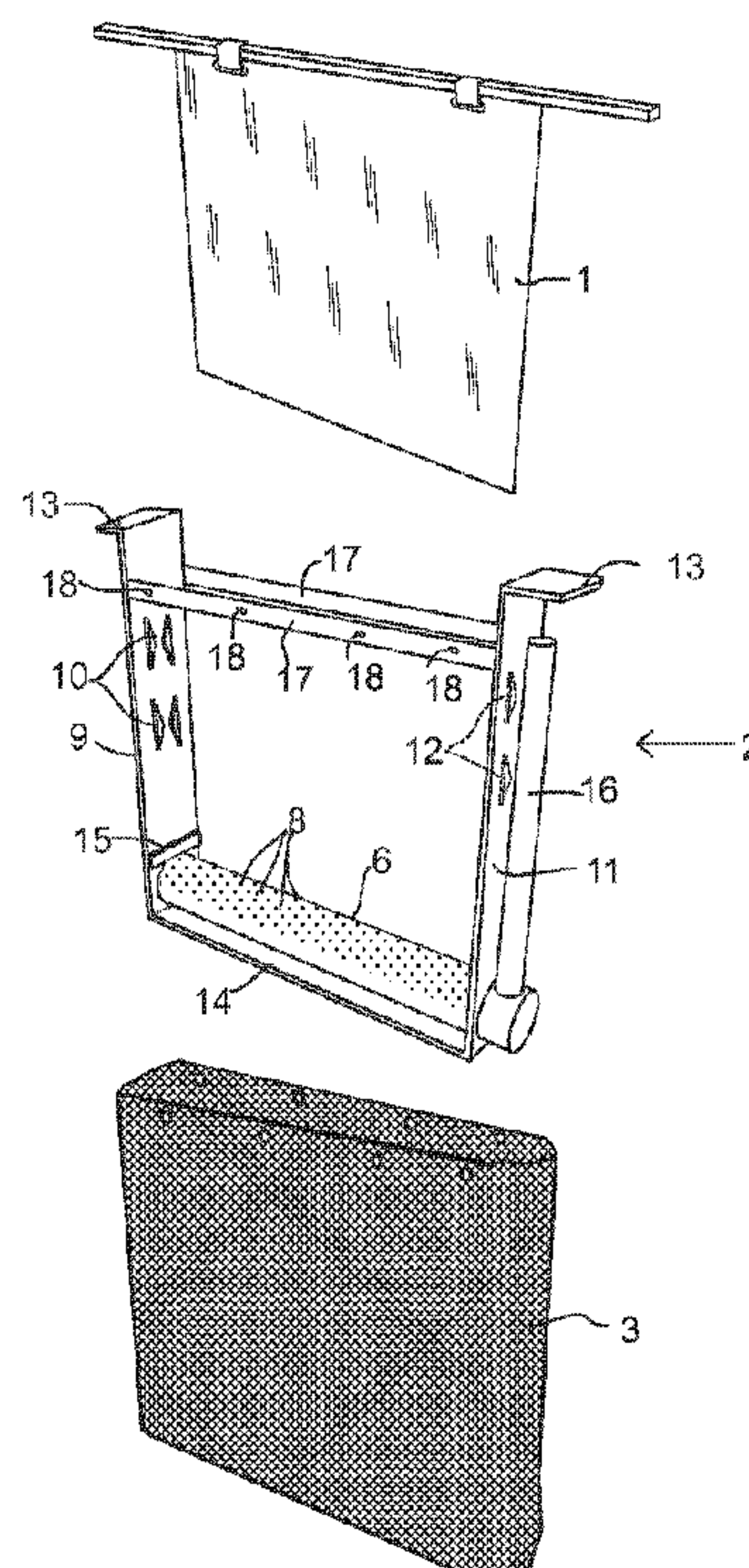


(86) Date de dépôt PCT/PCT Filing Date: 2013/02/06
(87) Date publication PCT/PCT Publication Date: 2013/08/15
(45) Date de délivrance/Issue Date: 2016/07/05
(85) Entrée phase nationale/National Entry: 2014/07/07
(86) N° demande PCT/PCT Application No.: FI 2013/050128
(87) N° publication PCT/PCT Publication No.: 2013/117814
(30) Priorité/Priority: 2012/02/08 (FI20125139)

(51) Cl.Int./Int.Cl. *C25C 7/06* (2006.01),
C25B 13/00 (2006.01), *C25C 7/04* (2006.01)
(72) Inventeur/Inventor:
NIEMINEN, VILLE, FI
(73) Propriétaire/Owner:
OUTOTEC (FINLAND) OY, FI
(74) Agent: NORTON ROSE FULBRIGHT CANADA
LLP/S.E.N.C.R.L., S.R.L.

(54) Titre : PROCÉDE PERMETTANT DE FAIRE FONCTIONNER UNE CELLULE D'ELECTROLYSE ET CADRE DE CATHODE

(54) Title: METHOD OF OPERATING AN ELECTROLYSIS CELL AND CATHODE FRAME



(57) Abrégé/Abstract:

The invention relates to a method of operating an electrolysis cell in electrowinning of metal, wherein cathode plates (1) are arranged in cathode frames (2) and the cathode plate and cathode frame are enclosed in a diaphragm bag (3) so as to form a cathode bag assembly, and the cathode bag assemblies and anode plates (4) are arranged in the electrolyte in an electrolysis cell (5) in an alternating and consecutive manner. A gas-sparging means (6) is disposed in each of the cathode bag assemblies, and sparging gas is supplied to the gas-sparging means (6) such that the gas-sparging means forms a curtain of fine sparging gas bubbles to flush the cathode plate (1). The cathode frame (2) comprises a gas—sparging means (6) for flushing the cathode plate (1) with a curtain of fine sparging gas bubbles inside the cathodic compartment.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau(10) International Publication Number
WO 2013/117814 A1(43) International Publication Date
15 August 2013 (15.08.2013)

(51) International Patent Classification:

C25C 7/06 (2006.01) C25B 13/00 (2006.01)
C25C 7/04 (2006.01)

(21) International Application Number:

PCT/FI2013/050128

(22) International Filing Date:

6 February 2013 (06.02.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

20125139 8 February 2012 (08.02.2012) FI

(71) Applicant: OUTOTEC OYJ [FI/FI]; Riihitontuntie 7, FI-02200 Espoo (FI).

(72) Inventor: NIEMINEN, Ville; Kuuratie 4, FI-28300 Pori (FI).

(74) Agent: PAPULA OY; P.O.Box 981, FI-00101 Helsinki (FI).

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

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: METHOD OF OPERATING AN ELECTROLYSIS CELL AND CATHODE FRAME

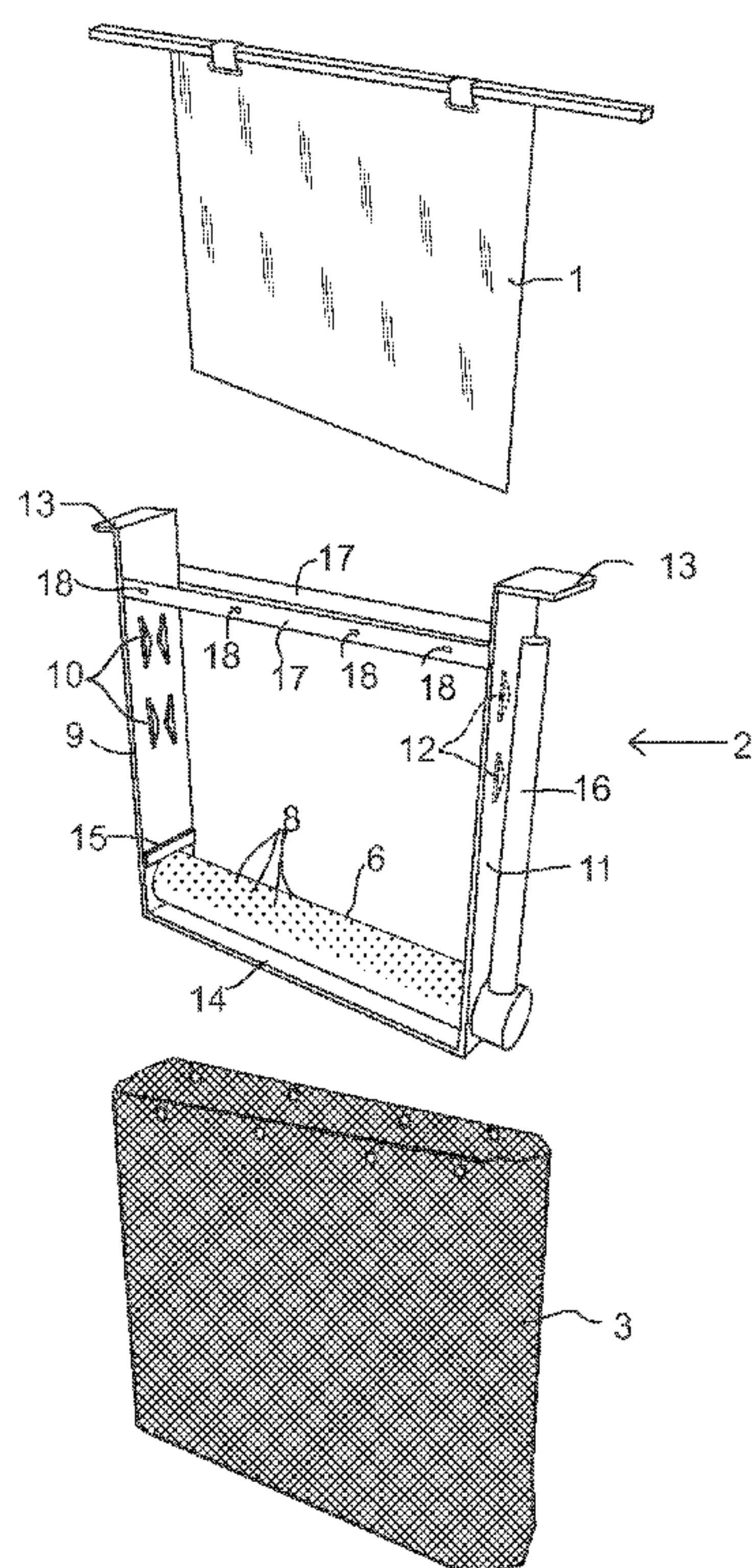


Fig. 1

(57) Abstract: The invention relates to a method of operating an electrolysis cell in electrowinning of metal, wherein cathode plates (1) are arranged in cathode frames (2) and the cathode plate and cathode frame are enclosed in a diaphragm bag (3) so as to form a cathode bag assembly, and the cathode bag assemblies and anode plates (4) are arranged in the electrolyte in an electrolysis cell (5) in an alternating and consecutive manner. A gas-sparging means (6) is disposed in each of the cathode bag assemblies, and sparging gas is supplied to the gas-sparging means (6) such that the gas-sparging means forms a curtain of fine sparging gas bubbles to flush the cathode plate (1). The cathode frame (2) comprises a gas-sparging means (6) for flushing the cathode plate (1) with a curtain of fine sparging gas bubbles inside the cathodic compartment.

WO 2013/117814 A1



Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *of inventorship (Rule 4.17(iv))*

Published:

- *with international search report (Art. 21(3))*

METHOD OF OPERATING AN ELECTROLYSIS CELL AND CATHODE FRAME

FIELD OF THE INVENTION

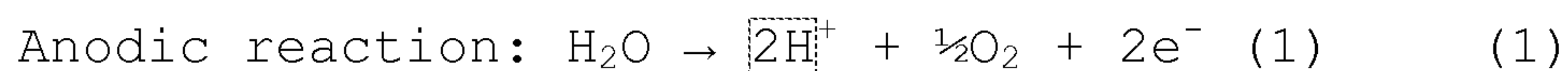
5 The present invention relates to a method of operating an electrolysis cell in electrowinning of metal, wherein cathode plates are arranged in cathode frames. The cathode plate and the cathode frame are enclosed in a diaphragm bag so as to form a cathode bag assembly.
 10 bly. The cathode bag assemblies and anode plates are arranged in the electrolyte in an electrolysis cell in an alternating and consecutive manner. Further, the invention relates to a cathode frame configured to retain a cathode plate and a diaphragm bag which encloses
 15 es said cathode plate inside said cathode frame to form a cathodic compartment inside the diaphragm bag.

BACKGROUND OF THE INVENTION

Electrowinning is a process where a metal dissolved in
 20 an electrolyte is reduced on a cathode by means of electric current. Electrowinning takes place in an electrolytic cell that contains a number of anodes and a number of cathodes arranged in an alternating manner.

25

When an electric current is conducted to the electrolysis system, metal is precipitated on the surface of the cathode and oxygen is generated on the anodes when the water decomposes, acid and oxygen are formed on
 30 the anodes, according to the reaction equations (1) and (2):



35

Me = metal, such as Ni, Co, Mn or Cu

wherein z = the charge of a metal ion

A diaphragm technique can be used in electrowinning metals, which in the electrochemical series are less noble than hydrogen, eg. Ni, Co, Mn. The overpotential of the reduction of these metals is higher than that of hydrogen, which is why the development of hydrogen at a low pH should be avoided by separating the anolyte and the catholyte from each other by a material that permeates the electrolyte in a controlled manner, such as a diaphragm fabric, and the electrolyte should flow from the catholyte compartment to the anolyte compartment.

Typically, in sulphate-based nickel, manganese and cobalt electrowinning, said metal can be recovered using divided-cell electrowinning technology, i.e. where the anode and cathode compartments in the cell are separated appropriately. In such tankhouses, the solution surrounding the cathode (catholyte) is separated from the adjacent anodes in the cell by slotting each cathode into a suitable frame, over which a bag of diaphragm material is stretched. The diaphragm material of the bag permeates the electrolyte in a controlled manner.

A typical target in nickel electrowinning is to have a high $\Delta\text{-Ni}$ (also known as bite i.e. difference in Ni concentrations between the electrolyte fed to the electrolysis cell and electrolyte overflowed from the cell), or a high anolyte sulfuric acid concentration. The higher the $\Delta\text{-Ni}$, the more economic is the process since no excess circulation in the leaching SX-EW-circuit exists. When said cathode bag technology (cathodes are in bags in order to keep catholyte pH high enough for the Ni-EW process) is used, $\Delta\text{-Ni}$ can be increased by two ways, by

1) increasing the current density

2) decreasing the electrolyte flow rate to the cathode bag and consequently through the diaphragm used to separate anodic and cathodic compartment from each other.

5

In nickel electrowinning, increasing current density is limited at the typical industrial conditions and not much higher than 200 A/m² can be used without serious problems in cathode quality. Increasing current density causes increased nodular growth of metal at the lower end of the cathode. Heavy nodular growth may tear the bag. A torn bag allows acid to migrate into the catholyte compartment thus suppressing the pH to a level at which hydrogen is produced. This causes pitting on the cathode surface resulting in a rough surface. Hydrogen formation causes also a risk of explosion. Nodular growth of the cathode tearing the bag may also cause a shortcut to the neighboring anode thereby decreasing the current efficiency.

20

Another possibility is to decrease the electrolyte flow through the diaphragm bags. However, when cathode bags are used this option is not possible since it is difficult to distribute even flow over the tankhouse and in addition, the electrolyte retention time inside the diaphragm bag would be very long and electrolyte flow/circulation (inside the bag) would be too slow. Also temperature control is difficult with slow electrolyte flow.

30

In prior art, as is known from documents WO 2005/019502 A1, US 3,959,112, US 6,849,172 B2 and article "Gas bubble induced mixing in electrowinning baths" G. D. Rigby; P. E. Grazier, A. D. Stuart, E. P. Smithson; Chemical Engineering Science 56 (2001) 6329-6336, gas-sparging has been utilized in copper electrowinning to obtain higher current density and to

35

produce high quality metal cathode. It is known that the gas bubbles arising along the electrode surface decrease the Nernst diffusion layer and thereby increase the limiting current density (and the critical
5 current density). Thereby a higher current density is possible to be used without decreasing the surface quality of the deposit on the electrode. Typically, in prior art, a gas-sparging manifold has been arranged at the bottom of the electrolysis cell. However, this
10 kind of arrangement of the gas-sparging manifold at the bottom of the cell is not usable in the cathode bag technology since the diaphragm prevents the bubbles from reaching the cathode.

15 Therefore, an object of the present invention is to alleviate the problems described above and to introduce a method of operating an electrolysis cell and a cathode frame that allow the electrowinning to be operated at a high current density and at the same time
20 to achieve a high quality cathode deposit with a smooth surface and with a minimum amount of nodular growth.

Further, the object of the invention is to introduce a
25 method of operating an electrolysis cell and a cathode frame that allow to achieve a high ΔMe (difference in the metal concentrations between the electrolyte fed to the cell and electrolyte overflown from the cell) whereby less cells are needed to obtain the
30 same capacity.

Further, the object of the invention is to introduce a method of operating an electrolysis cell and a cathode frame that minimize the number of torn cathode bags
35 and short-cuts and therefore to achieve a high current efficiency.

Further, the object of the invention is to introduce a method of operating an electrolysis cell and a cathode frame that allow a good mixing of the electrolyte resulting in a homogenous electrolyte inside the cathode bag.

SUMMARY OF THE INVENTION

A first aspect of the present invention is a method of operating an electrolysis cell in electrowinning of metal, wherein cathode plates are arranged in cathode frames and the cathode plate and cathode frame are enclosed in a diaphragm bag so as to form a cathode bag assembly, and the cathode bag assemblies and anode plates are arranged in the electrolyte in an electrolysis cell in an alternating and consecutive manner. According to the invention the method includes disposing a gas-sparging means in each of the cathode bag assemblies, and supplying sparging gas to the gas-sparging means such that the gas-sparging means forms a curtain of fine sparging gas bubbles to flush the cathode plate.

A second aspect of the present invention is a cathode frame configured to retain a cathode plate and a diaphragm bag which encloses said cathode plate inside said cathode frame to form a cathodic compartment inside the diaphragm bag. According to the invention the cathode frame comprises a gas-sparging means for flushing the cathode plate with a curtain of fine sparging gas bubbles inside the cathodic compartment.

The advantage of the invention is that the sparged gas bubbles arising along the cathode plate surfaces decrease the Nernst diffusion layer and thereby increase the limiting current enabling a high current density. With the high current density, a high delta-Me or anolyte acid concentration can be achieved and less

electrolytic cells leading to a lower capital expenditure for the tankhouse. Despite the high current density it is possible to achieve a very smooth cathode deposit surface, i.e. high quality cathode is
5 achieved. Nodular growth and torn bags are significantly reduced thereby reducing the number of short-cuts and leading to a high current density and low operating expenses. The bubbles also improve mixing of electrolyte inside the diaphragm bag.

10

In an embodiment of the invention, the method further includes disposing an electrolyte feed means in each of the cathode bag assemblies, and supplying electrolyte to the electrolyte feed means to feed electrolyte
15 into the cathode bag. The gas-sparging allows that electrowinning can be operated at a high current density and therefore the electrolyte feed does not need to be excessively reduced in order to achieve a high delta-Me.

20

In an embodiment of the invention, the gas-sparging means comprises a gas delivery manifold with a plurality of outlet orifices, said gas delivery manifold being located at a distance below the cathode plate.

25

In an embodiment of the invention, the cathode frame comprises an electrolyte feed means integrated to the cathode frame for feeding of the electrolyte into the cathodic compartment.

30

In an embodiment of the invention, the electrolyte feed means comprises an electrolyte feed manifold located adjacent the gas delivery manifold.

35

In an embodiment of the invention, the electrolyte feed manifold is located below the gas delivery manifold.

In an embodiment of the invention, the cathode frame comprises

- 5 - a vertical first side member having an upper end and a lower end,
- a first guide arranged at the first side member between the upper end and the lower end of the first side member to provide vertical guidance and lateral support for a first edge of the cathode plate,
- 10 - a vertical second side member at a distance from the first side member, said second side member having an upper end and a lower end,
- a second guide arranged at the second side member between the upper end and the lower end of the first side member to provide vertical guidance and lateral support for a second edge of the cathode plate,
- 15 - hangers at the upper ends of the first and second side member, said hangers being adapted to hang the cathode frame to the support of the opposite walls of the electrolysis cell, and
- 20 - a horizontal bottom member extending between and rigidly connecting the lower ends of the first and second side members, whereby the gas delivery manifold is arranged to extend between the side members on and along the bottom member.
- 25

In an embodiment of the invention, the cathode frame comprises a stop member arranged at each of the first and second side members, against which stop members the lower end of the cathode plate may abut, said stop members being arranged to keep the lower end of the cathode plate at a distance from the gas delivery manifold

In an embodiment of the invention, the cathode frame comprises gas inlet channel arranged to supply pressurized gas to the gas delivery manifold.

5 In an embodiment of the invention, the gas outlet orifices are disposed at the upper part of the gas delivery manifold to direct the delivery of bubbles to an upwards direction. The aim is that all gas bubbles go directly upwards so that collisions and fusion of gas
10 bubbles to larger bubbles on the gas delivery manifold are prevented so as to maintain the small size of the gas bubbles.

In an embodiment of the invention, the first guide and
15 the second guide are disposed to center the cathode plate in the middle of the gas delivery manifold so that substantially an equal amount of fine bubbles uniformly flush each one of the opposite surfaces of the cathode plate.

20

In an embodiment of the invention, the cathode frame comprises a pair of cross-bars arranged adjacent the upper end of the cathode frame, each one of said cross-bars having a first end connected to the first
25 side member and the a second end connected to the second side member.

In an embodiment of the invention, the cross-bars comprise fastening members by which the diaphragm bag can
30 be releasably fastened to the cathode frame.

In an embodiment of the invention, the gas delivery manifold is a gas permeable tube, the lower part of the tube being deposited with a gas impermeable material.
35

In an embodiment of the invention, the gas permeable upper part of the gas permeable tube is covered with material which improves the breakdown of the bubbles discharged from the orifices to smaller bubbles.

5

In an embodiment of the invention, the cathode frame comprises a cap which is releasably and gas-tightly connectable to the cathode frame, and that the cap comprises a central slot through which the cathode
10 plate is sealably insertable to and removable from the frame.

In an embodiment of the invention, the cap comprises a suction pipe for removal of the sparged gas from in-
15 side the bag.

The method and the cathode frame having the gas-sparging means according to the invention can be used in any electrowinning process that needs separation of
20 the catholyte (electrolyte inside the cathode bag) and the anolyte (electrolyte in the cell space surrounding the cathode bags). Thus, the method and the cathode frame of the invention are usable in the electrowinning of nickel, manganese and cobalt. Further,
25 the method and the cathode frame are also usable in the electrowinning of copper. Further, it is also usable in the electrowinning of gold and silver.

It is to be understood that the aspects and embodi-
30 ments of the invention described above may be used in any combination with each other. Several of the aspects and embodiments may be combined together to form a further embodiment of the invention. A method for electrowinning or a cathode frame which is an aspect
35 of the invention may comprise at least one of the embodiments of the invention described above.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are included to provide a further understanding of the invention and constitute a part of this specification, illustrate
5 embodiments of the invention and together with the description help to explain the principles of the invention. In the drawings:

Fig. 1 schematically shows an exploded view of a cathode bag assembly including a cathode frame according
10 to one embodiment of the invention, a cathode plate insertable to the frame and a diaphragm bag configured to be drawn on the frame;

15 Fig. 2 shows one embodiment of the cathode bag assembly assembled from the parts shown in Fig. 1;

Figs. 3 shows another embodiment of the cathode frame having both the gas-sparging and electrolyte feed
20 means integrated into the cathode frame;

Fig. 4 schematically shows a cross-sectional view of the cathode bag assembly immersed in the electrolyte and the gas-sparging means sparging fine bubbles along
25 the cathode plate surfaces;

Fig. 5 shows a cross-section of the gas delivery manifold of one embodiment of the invention;

30 Fig. 6 schematically shows an electrolysis cell equipped with the cathode bag assemblies having cathode frames of Fig. 2 and anode plates arranged in the cell.

DETAILED DESCRIPTION OF THE INVENTION

Reference will now be made in detail to the embodiments of the present invention, examples of which are illustrated in the accompanying drawings.

5

Figure 1 shows a cathode frame 2 which is configured to hold a cathode plate 1 and a diaphragm bag 3. In Figure 1 cathode plate 1 and the diaphragm bag 3 are shown separate from the cathode frame 2. The cathode
10 frame 2 with the cathode plate 1 installed in the cathode frame 2 can be inserted inside the diaphragm bag 3 so that the diaphragm bag 3 encloses the cathode frame in a manner as shown in Fig. 2. The cathode plate 1 can be either a starter sheet or a permanent
15 cathode.

The cathode frame 2 comprises a gas-sparging means 6. The gas-sparging means comprises a gas delivery manifold 6 having a plurality of outlet orifices 8 through
20 which the sparging gas can be distributed to the electrolyte in the cathodic compartment inside the diaphragm bag 3 as a cloud of fine bubbles which rise as a curtain along the surface of the cathode plate 1 as illustrated in Fig. 4. Pressurized gas may be supplied
25 to the gas delivery manifold 6 via a gas inlet channel 16. The gas outlet orifices 8 are disposed at the upper part of the gas delivery manifold 6 to allow bubble delivery only in an upwards direction. The gas outlet orifices 8 have a diameter smaller than 3 mm.

30

With reference to Fig. 5, in one example, the gas delivery manifold 6 may be made of a gas permeable tube, so that only the lower part of the tube is deposited with a gas impermeable material 19 and the upper part
35 of the tube is left undeposited for discharging the sparging gas in an upwards direction. The gas impermeable material 19 can be any suitable gas impermeable

material, such as a layer of paint, lacquer, glue or polymer. The gas permeable upper part of the gas permeable tube 6 may also be covered with material 24, such as industrial fabric, which improves the breakdown of the bubbles discharged from the orifices 8 to even smaller bubbles.

Referring to Fig. 1, the cathode frame 2 comprises a vertical first side member 9 having an upper end and a lower end. A first guide 10 is arranged at the first side member 9 between the upper end and the lower end of the first side member to provide vertical guidance and lateral support for a first edge of the cathode plate. The cathode frame 2 comprises a vertical second side member 11 at a distance from the first side member, said second side member having an upper end and a lower end. A second guide 12 is arranged at the second side member 11 between the upper end and the lower end of the first side member to provide vertical guidance and lateral support for a second edge of the cathode plate. A horizontal bottom member 14 extends between and rigidly connecting the lower ends of the first and second side members 9, 11 so that the cathode frame 2 is substantially a U-shaped rigid structure. The cathode frame 2 can be made of suitable polymer material reinforced with steel inside the polymer material.

The gas delivery manifold 6 extends between the side members 9, 11 on and along the bottom member 14. The cathode frame 2 comprises a stop member 15 which is arranged oppositely at the first and second side members 9, 11 so that the lower end of the cathode plate 1 may abut against the stop members 15. The stop members 15 being are arranged to keep the lower end of the cathode plate at a distance h from the gas delivery manifold 6 so that the cathode plate 2 never contacts the gas delivery manifold 6 when the cathode

plate 1 is installed in the cathode frame 2 (see Figs. 2 and 4).

As shown in Fig. 2 and Fig. 4, the first guide 10 and the second guide 12 are disposed to center the cathode plate 1 in the middle of the gas delivery manifold 6 so that substantially an equal amount of fine bubbles uniformly flush each one of the opposite surfaces of the cathode plate 1.

10

As shown in Figs 1, 2, and Fig 6, the cathode frame 2 comprises a pair of hangers 13 at the upper ends of the first and second side member 9. 11. The hangers are adapted to hang the cathode frame 2 to the support of the opposite walls of the electrolysis cell 5.

15

As shown in Figs. 1 and 2, the cathode frame 2 may also comprise a pair of cross-bars 17 arranged adjacent the upper end of the cathode frame 2. The number of cross-bars can also more than two, if needed. The cross-bars 17 have a first end connected to the first side member 9 and a second end connected to the second side member 11. The cross-bars 17 strengthen the structure of the cathode frame 2.

20

25

The cross-bars 17 may also serve in fastening the diaphragm bag to the frame 2. Then the cross-bars 17 may comprise fastening members 18 by which the diaphragm bag 3 can be releasably fastened to the cathode frame 2. For example, the fastening members 18 may comprise a plurality of lugs to which the diaphragm bag 3 can be hanged, as shown in Fig. 2. In another embodiment the fastening members 18 can be e.g. cable ties or like straps (not shown) by which the diaphragm bag 3 can be hanged to the cross-bars 17. Also any other way known to the man skilled in the art may be used for of fastening the diaphragm bag to the cathode frame.

30

35

Fig. 3 shows a further modification of the cathode frame 2 of Fig. 1. In this embodiment the cathode frame 2 comprises a gas-sparging means 6 as disclosed above with reference to Fig. 1, 2, 3 and 5, and also an electrolyte feed means 7 integrated to the cathode frame 2 for feeding of the electrolyte into the cathodic compartment inside the bag 3. The electrolyte feed means comprises an electrolyte feed manifold 7 located adjacent and below the gas delivery manifold 6. As an alternative to Fig. 3, the gas delivery manifold 6 of Fig. 1 can also be used to deliver electrolyte into the bag 3. A simultaneous feeding of both sparging gas and electrolyte via the gas delivery manifold 6 is also possible.

In another embodiment (not shown in Figs.) the gas delivery manifold 6 (and the electrolyte feed manifold 7 and the bottom member 14 of the frame 2 are all integrated into an integral structure. The side members 9, 11 may also include shading elements that shade the flow so that the metal precipitating on the cathode surface does not grow on edge regions of the cathode plate 1 and get stuck with the guides 12.

Fig. 4 shows that the cathode frame 2 may also comprise a cap 20 which is releasably and gas-tightly connectable to top of the cathode frame 2. The cap 20 comprises a central slot 21 through which the cathode plate 1 is sealably insertable to and removable from the frame. The sparged gas which is collected to a space limited by the cap 20 and the electrolyte surface may be suctioned by a suction pipe 22 for removal of the sparged gas from inside the bag 3.

With reference to Fig. 6, the arrangement as disclosed above with reference to Figs. 1 to 5, is used in elec-

trowinning of metal, wherein cathode plates 1 are arranged in cathode frames 2 and the cathode plate and cathode frame are enclosed in a diaphragm bag 3 so as to form a cathode bag assembly as shown on Fig. 2. These cathode bag assemblies and anode plates 4 are arranged in the electrolyte in an electrolysis cell 5 in an alternating and consecutive manner. The necessary busbars arranged to supply electric current are not shown in Fig. 6. The busbars may be arranged in any way known to a man skilled in the art. Sparging gas is supplied to the gas-sparging means 6 such that a curtain of fine sparging gas bubbles is formed to flush the cathode plate 1. Also electrolyte may be supplied to the electrolyte feed means 7 to feed electrolyte into the cathode bag assembly. A tube 23 for supplying and distributing sparging gas, resp. electrolyte, to the gas-sparging means 6, resp. to electrolyte feed means 7, is preferable disposed outside the cell 5 beside the side wall of the cell as schematically illustrated in Fig. 6.

Example

In order to show the effects of gas-sparging in conjunction with cathode frame tests were conducted in a laboratory scale electrolysis cell configured for nickel electrowinning. Air was used as the sparging gas. The current density was 300 A/m^2 while normally in the nickel electrowinning a current density much more than 200 A/m^2 cannot be used without problems in cathode quality when the arrangement of the invention is not used. The cathode frame having a structure as shown in Fig. 1 was used in tests. The gas delivery manifold in the bottom of the cathode frame was made of soaking hose which is a porous air permeable tube. The soaking hose was treated with gas impermeable glue substantially in the manner as disclosed with reference to Fig. 4 so that the air bubbles would be re-

leased upwards from the upper part of the hose. The frame was equipped with an air inlet pipe to supply air to the gas delivery hose and cathode guides/holders to keep the cathode in position under sparging and stoppers that kept the bottom edge of the cathode from a distance of the hose. The cell was accommodated in a water bath to keep the electrolyte temperature constant. Catholyte was pumped into the cell (volume 3.5 l) inside a diaphragm bag that isolated catholyte from the anolyte. Anolyte was collected as overflow. A nickel starter sheet was used as a cathode and two anodes were Pb-Ag (Ag 0.5%) (size 7.8 cm x 9.0 cm) with the spacing between anodes of 110 mm and hydrostatic head of 20 mm. Hydrostatic head is the height difference between anolyte surface and catholyte surface (see also Fig. 4; Catholyte surface is at a higher level than the anolyte surface and therefore the flow of the electrolyte is in the direction from the cathodic compartment (inside cathode bag) to the anodic compartment (outside cathode bag)). Air was sparged 300 ml/min and 2.2 g/l Na-laurylsulfate was used as an additive. The nickel cathodes produced at 300 A/m² had very smooth surfaces. No pitting on the cathode surfaces due to the hydrogen formation was present demonstrating an additional beneficial effect of the air sparging in Ni-EW. Based on the experiment the current density can be increased by using the air sparging at least to 300 A/m² and very smooth deposit surface can be produced. Furthermore, no short-cuts were detected and it seems that gas sparging also reduces the tendency to obtain short circuits reducing the number of torn bags in the Ni-EW process.

A further modification of the invention may also be to integrate the gas-sparging means to an anode frame. The anode bag assembly comprises an anode frame into which an anode can be placed and a diaphragm bag is

installed to enclose these. A gas-sparging means may be integrated to the anode frame in a manner that the gas sparging means is located outside the anode bag so that the gas-sparging means may be positioned right
5 below the neighboring adjacent cathode plate to sparge gas as fine bubbles to flush the cathode plate.

While the present inventions have been described in connection with a number of exemplary embodiments, and
10 implementations, the present inventions are not so limited, but rather cover various modifications, and equivalent arrangements, which fall within the purview of prospective claims.

CLAIMS

1. A cathode frame (2) configured to retain a cathode plate (1) and a diaphragm bag (3) which encloses said cathode plate inside said cathode frame to form a cathodic compartment inside the diaphragm bag, the cathode frame (2) comprises a gas-sparging means (6) for flushing the cathode plate (1) with a curtain of fine sparging gas bubbles inside the cathodic compartment, the gas-sparging means comprising a gas delivery manifold (6) which is located at a distance (h) below the cathode plate (1), characterized in that gas delivery manifold (6) comprises a plurality of outlet orifices (8) disposed at the upper part of the gas delivery manifold (6) to allow bubble delivery in an upwards direction.

2. The cathode frame according to claim 1, characterized in that the cathode frame (2) comprises an electrolyte feed means (7) integrated to the cathode frame (2) for feeding of the electrolyte into the cathodic compartment.

3. The cathode frame according to claim 2, characterized in that the electrolyte feed means comprises an electrolyte feed manifold (7) located adjacent the gas delivery manifold (6).

4. The cathode frame according to claim 3, characterized in that the electrolyte feed manifold (7) is located below the gas delivery manifold (6).

5. The cathode frame according to any one of the claims 1 to 4, characterized in that the cathode frame (2) comprises

- a vertical first side member (9) having an upper end and a lower end,

- a first guide (10) arranged at the first side member between the upper end and the lower end of the first side member to provide vertical guidance and lateral support for a first edge of the cathode plate,
- 5 - a vertical second side member (11) at a distance from the first side member, said second side member having an upper end and a lower end,
- a second guide (12) arranged at the second side member between the upper end and the lower end of
10 the first side member to provide vertical guidance and lateral support for a second edge of the cathode plate,
- hangers (13) at the upper ends of the first and second side member, said hangers being adapted to
15 hang the cathode frame to the support of the opposite walls of the electrolysis cell, and
- a horizontal bottom member (14) extending between and rigidly connecting the lower ends of the first and second side members, whereby the gas deliv-
20 ery manifold (6) is arranged to extend between the side members (9, 11) on and along the bottom member (14).

6. The cathode frame according to claim 5, characterized in that the cathode frame (2) comprises
25 a stop member (15) arranged at each of the first and second side members (9, 11), against which stop members the lower end of the cathode plate may abut, said stop members being arranged to keep the lower end of the cathode plate at a distance (h) from the gas
30 delivery manifold (6)

7. The cathode frame according to claim 5 or 6, characterized in that the cathode frame (2) comprises a gas inlet channel (16) arranged to supply
35 pressurized gas to the gas delivery manifold (6).

8. The cathode frame according to any one of the claims 5 to 7, characterized in that the first guide (10) and the second guide (12) are disposed to center the cathode plate (1) in the middle of the gas delivery manifold (6) so that substantially an equal amount of fine bubbles uniformly flush each one of the opposite surfaces of the cathode plate.

9. The cathode frame according to any one of the claims 5 to 8, characterized in that the cathode frame (2) comprises a pair of cross-bars (17) arranged adjacent the upper end of the cathode frame, each one of said cross-bars having a first end connected to the first side member (9) and the a second end connected to the second side member (11).

10. The cathode frame according to claim 9, characterized in that the cross-bars (17) comprise fastening members (18) by which the diaphragm bag (3) can be releasably fastened to the cathode frame.

11. The cathode frame according to any one of the claims 1 to 10, characterized in that the gas delivery manifold (6) is a gas permeable tube, having a lower part of the tube which is deposited with a gas impermeable material (19).

12. The cathode frame according to claim 11, characterized in that the gas permeable upper part of the gas permeable tube (6) is covered with material (24) which improves the breakdown of the bubbles discharged from the orifices (8) to smaller bubbles.

13. The cathode frame according to any one of the claims 1 to 12, characterized in that the cathode frame (2) comprises a cap (20) which is releasably and gas-tightly connectable to the cathode

frame, and that the cap (20) comprises a central slot (21) through which the cathode plate (1) is sealably insertable to and removable from the frame.

5 14. The cathode frame according to claim 13, characterized in that the cap (20) comprises a suction pipe (22) for removal of the sparged gas from inside the bag.

10 15. Use of the cathode frame (2) according to any one of the claims 1 to 14 in the electrowinning of any one of the metals including nickel Ni, manganese Mn, cobalt Co, gold Au, silver Ag, copper Cu.

15

1/4

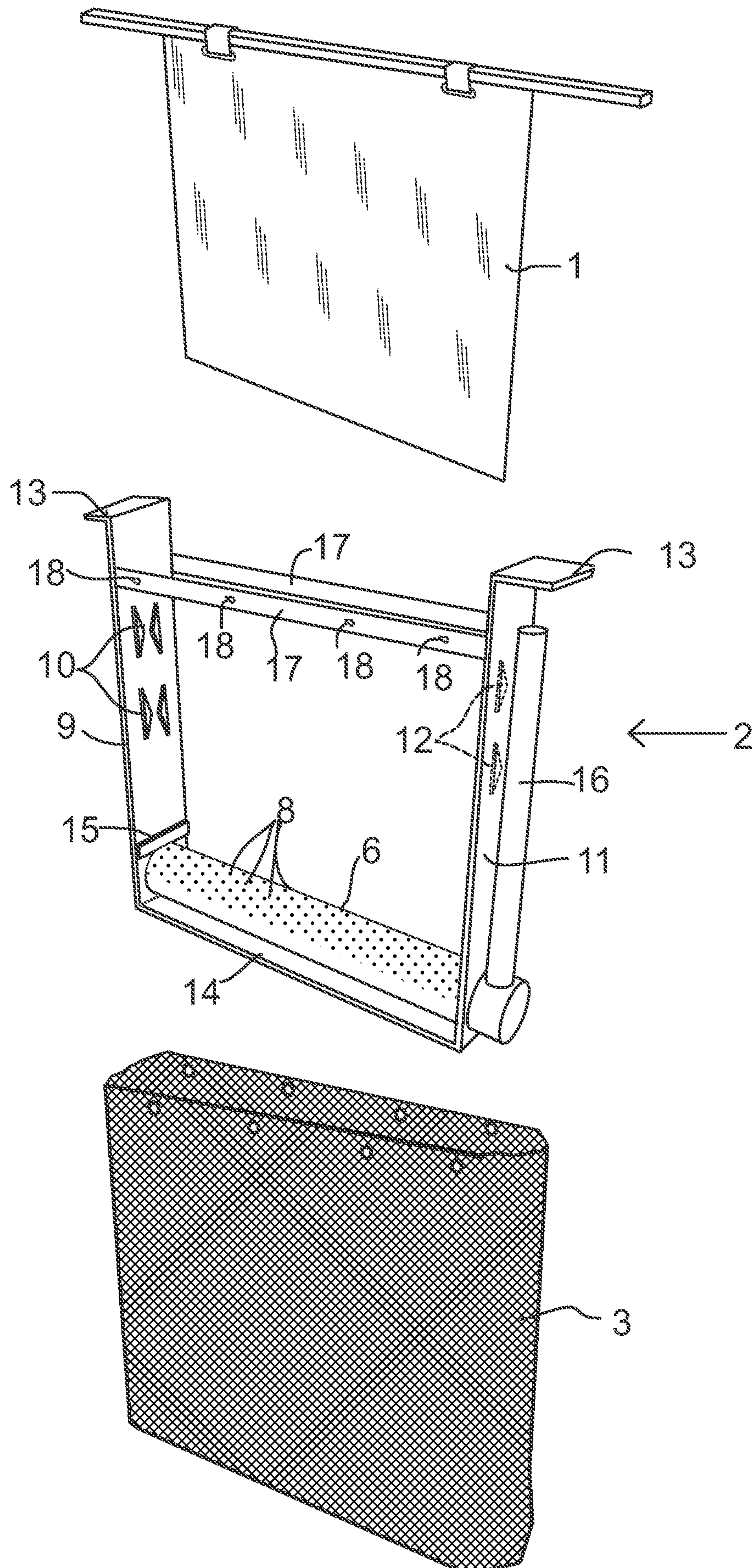


Fig. 1

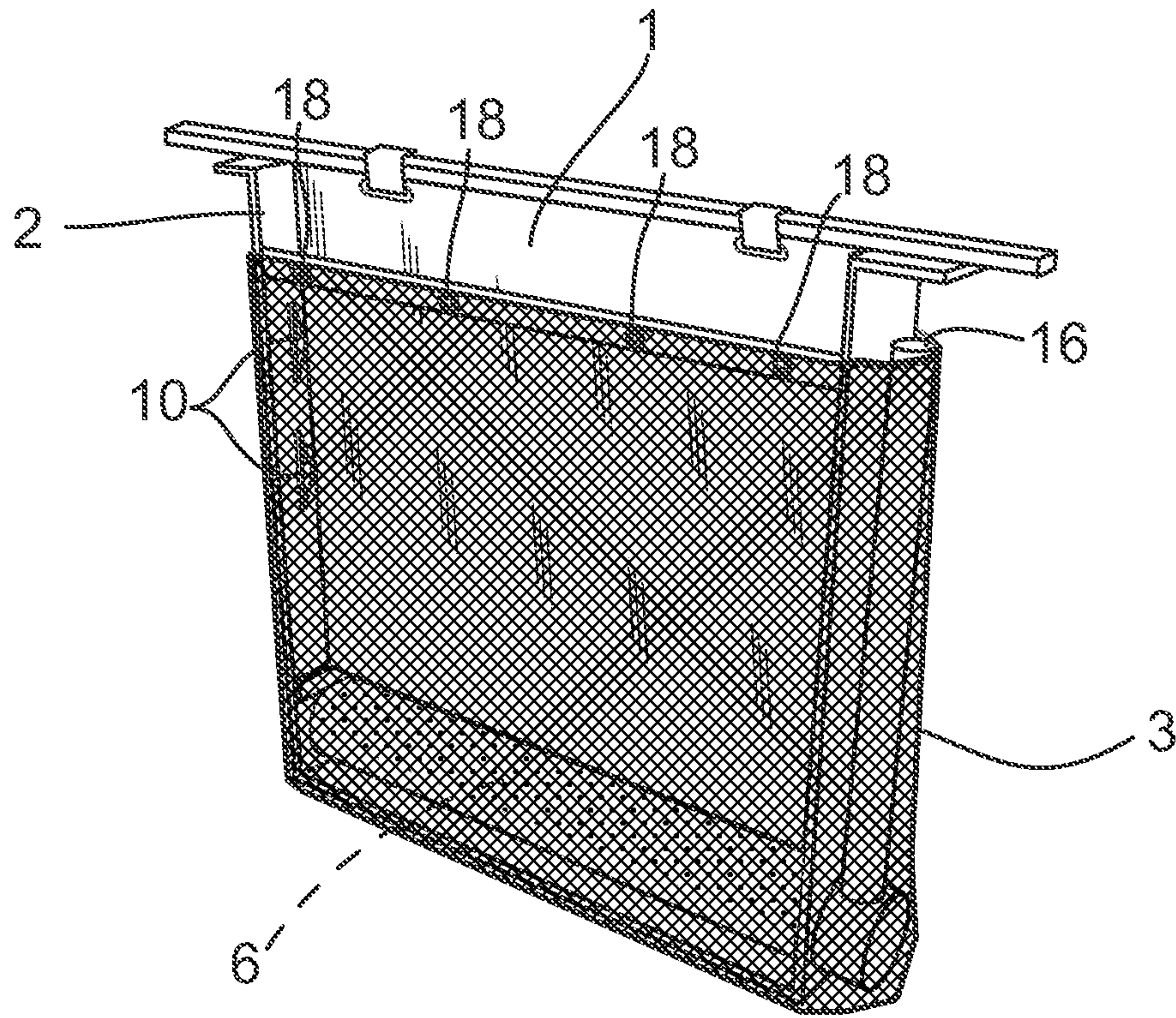


Fig. 2

3/4

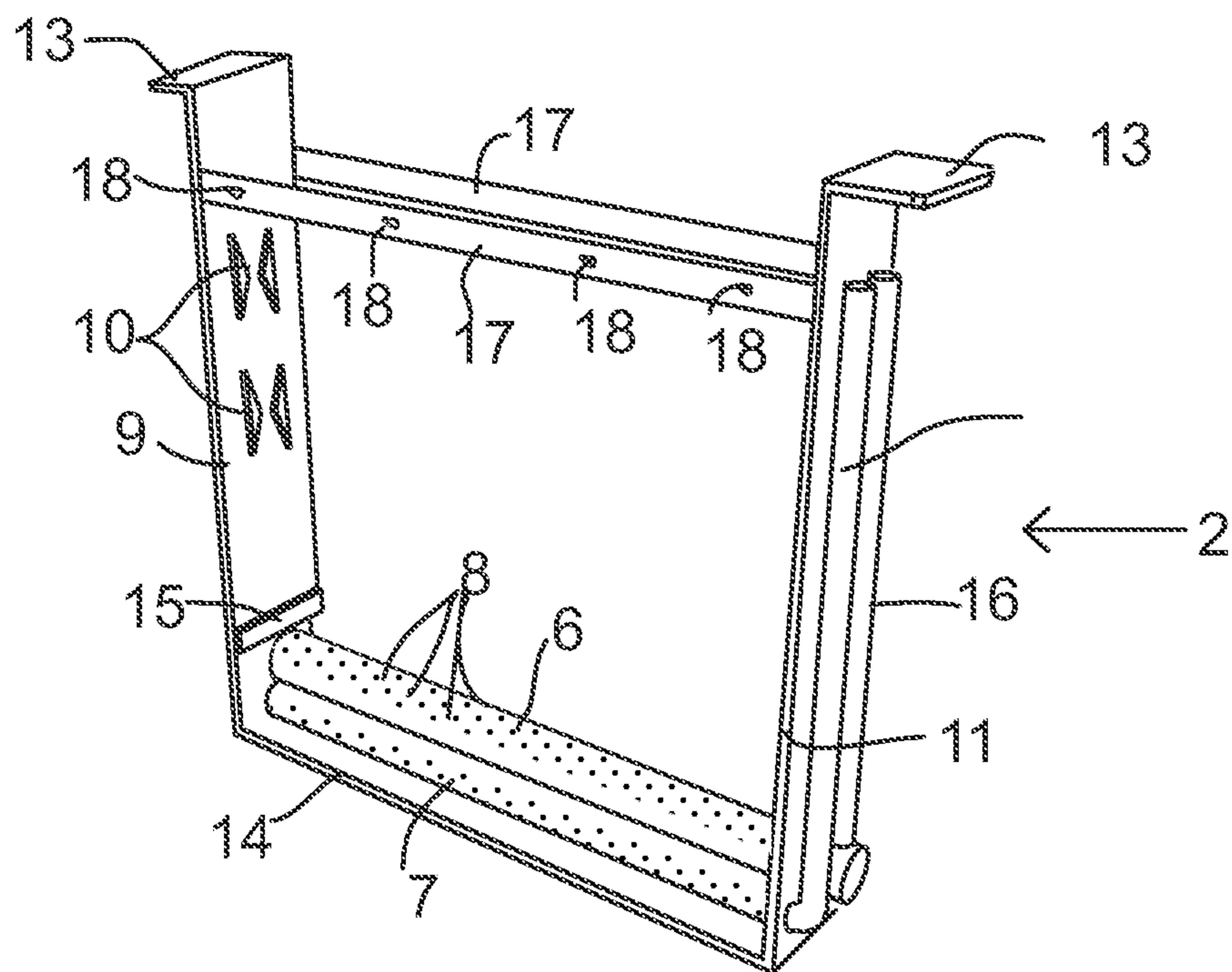


Fig. 3

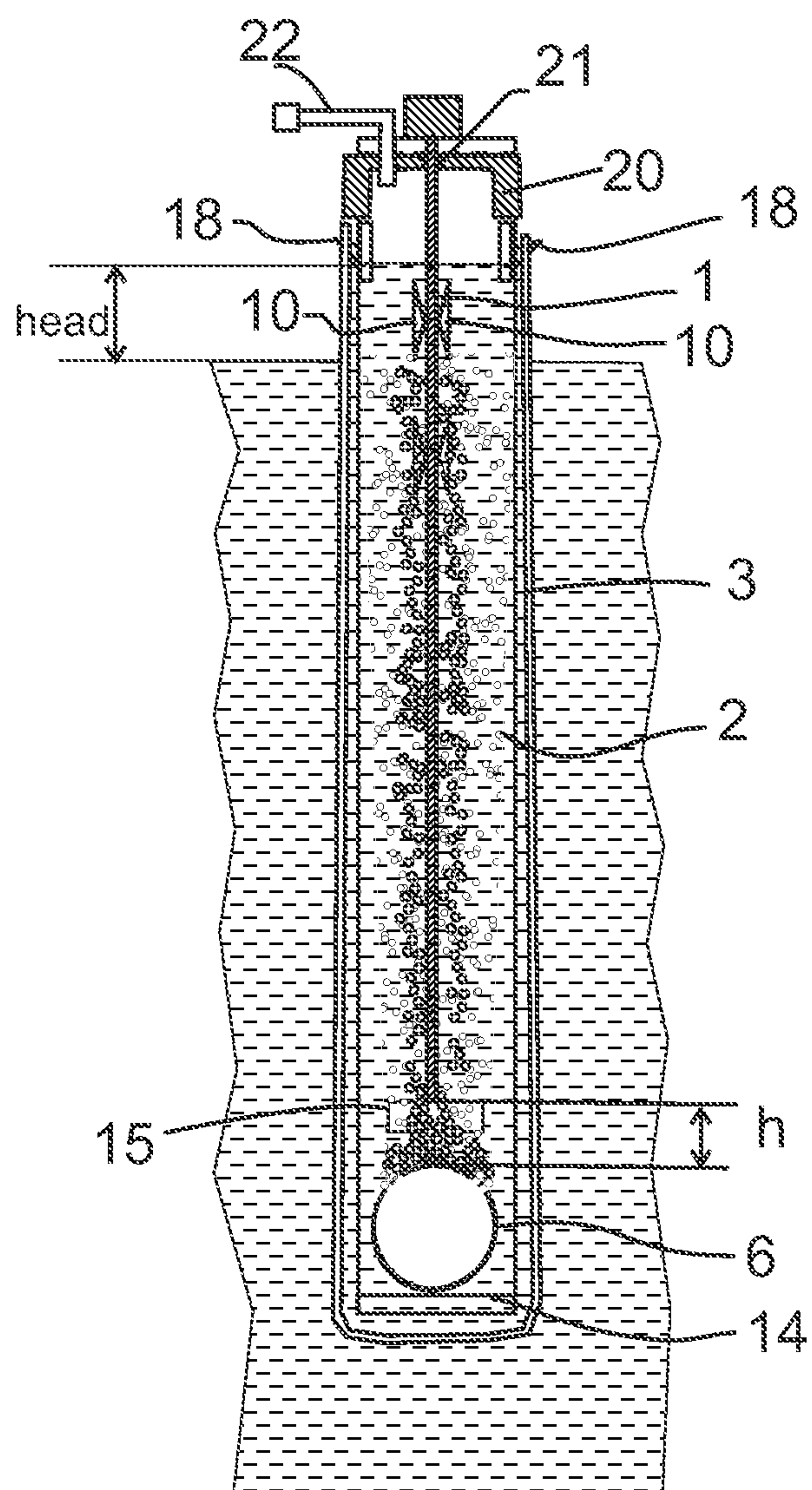


Fig. 4

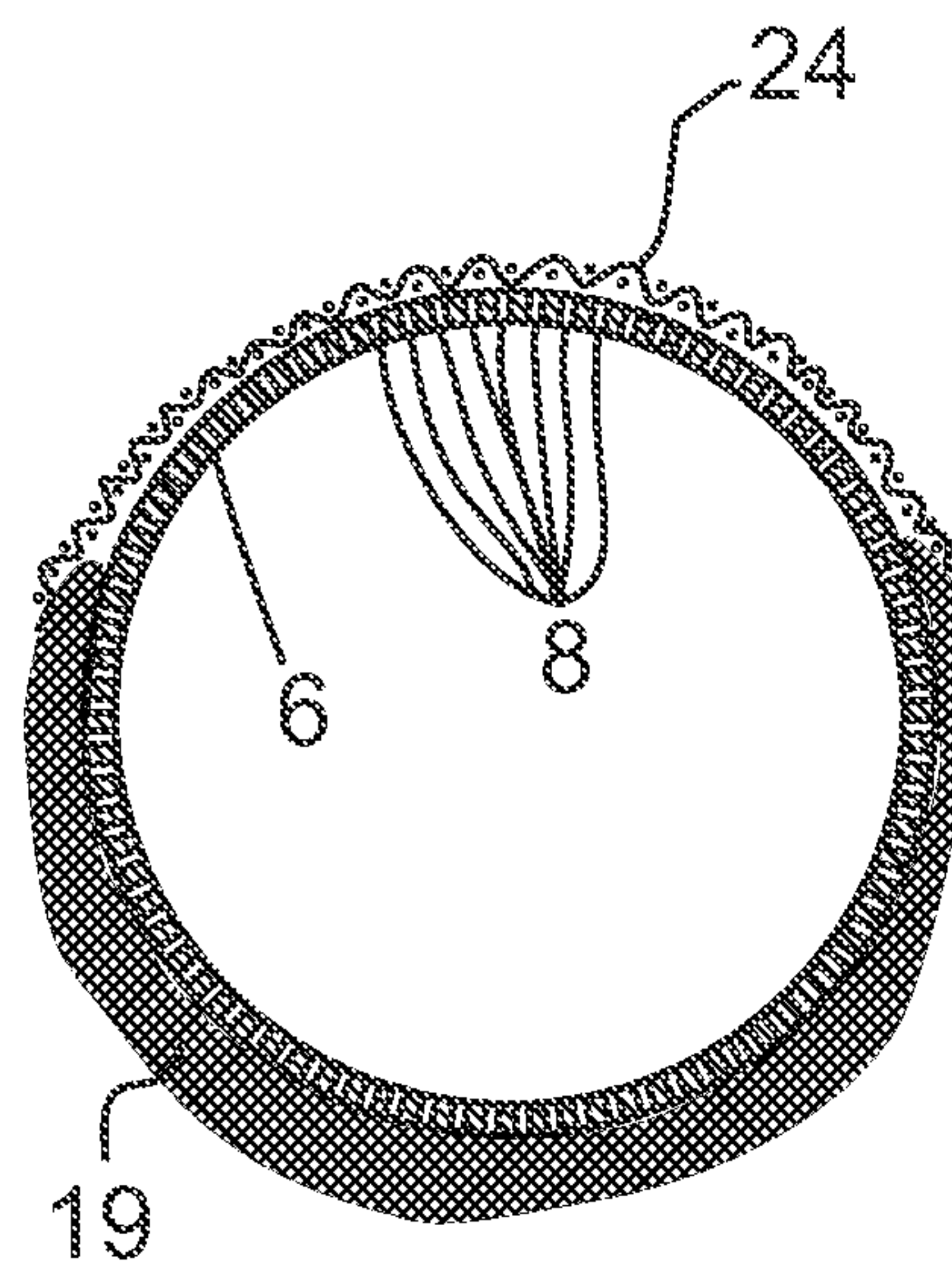


Fig. 5

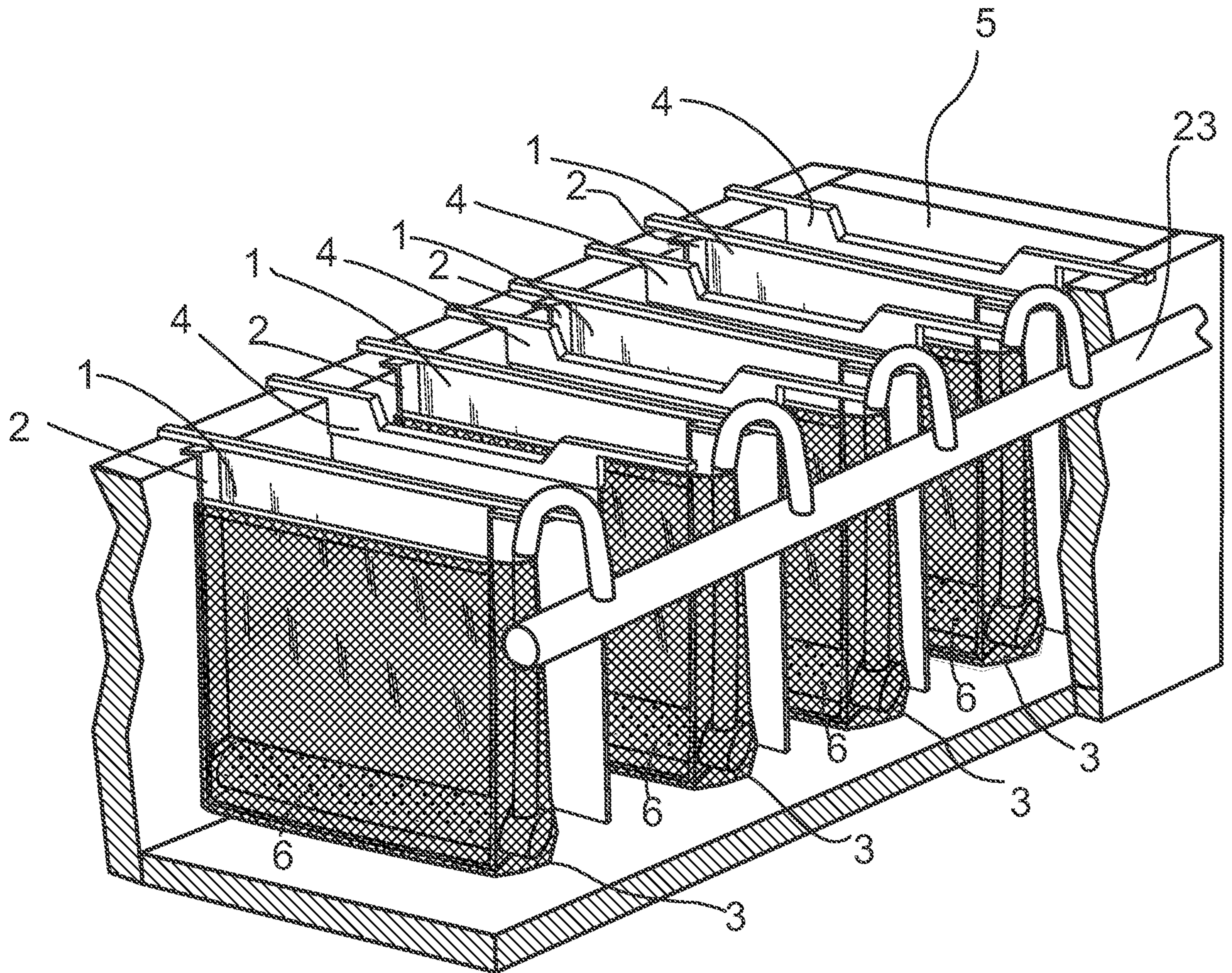


Fig. 6

