(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 242 337 B1**

(12) # EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification : **22.01.92 Bulletin 92/04**

(51) Int. Cl.^{5} : **C25D 21/18**

(21) Application number : **87830101.9**

(22) Date of filing : **18.03.87**

(54) **Apparatus for the continuous purification of electrolytes.**

(30) Priority : **20.03.86 IT 2128786 U**

(43) Date of publication of application : **21.10.87 Bulletin 87/43**

(45) Publication of the grant of the patent : **22.01.92 Bulletin 92/04**

(84) Designated Contracting States : **AT BE CH DE FR GB LI NL SE**

(56) References cited :
GB-A- 1 066 213
US-A- 3 926 754

(73) Proprietor : **Cortesi, Claudio**
Piazza Grandi, 5
I-20129 Milano (IT)

(72) Inventor : **Cortesi, Claudio**
Piazza Grandi, 5
I-20129 Milano (IT)

(74) Representative : **Cicogna, Franco**
Ufficio Internazionale Brevetti Dott.Prof.
Franco Cicogna Via Visconti di Modrone, 14/A
I-20122 Milano (IT)

EP 0 242 337 B1

Description

The present invention relates to apparatus for the continuous electrolytic purification of electrolytes, namely solutions utilised in electro-deposition processes and the like.

Unwanted metallic pollution inevitably occurs in solutions utilised for electro-deposition of metals (galvanic baths) and in solutions forming part of associated treatment cycles, which may for example be baths for degreasing, pickling, activation, passivation and the like. These solutions, in fact, have a tendency over a period of time to become contaminated with extraneous and unwanted metal ions from the workpieces under treatment or at other stages in the treatment cycle, from the superstructure of the installation and also from the accidental introduction of incorrect or impure chemical components.

The contamination of solutions by such unwanted ions is generally detrimental and removal is required, which is generally effected by chemical or electrolytic methods. Among the electrolytic methods currently being used, a distinction is made between those which effect purification directly in the vessel containing the contaminated solution, thereby interrupting production, and those which are performed outside the vessel itself, therefore permitting work to continue even whilst purification is being performed and which, consequently, are referred to as "continuous purification" methods.

Conventional apparatus used to effect continuous purification is comprised of a number of electrolytic cells of a particular form through which the solution to be purified is caused to flow by means of a pump. In such apparatus the purification takes place by electro-deposition at very low current density (normally from 0.1 to 0.5A per square decimetre). The extraneous metals present as contaminants are caused to deposit on the cathode at the lower limit of the range of current density normally employed for electro-deposition, the precise value depending on their position in the electrochemical series of elements and their concentration.

One known type of purification apparatus currently in use is essentially constituted by a cylindrical chamber or cell at the centre of which is positioned an insoluble cylindrical positive electrode (anode). At a certain distance from and concentric with the anode is a negative electrode (cathode). A current rectifier, which may or may not be connected with the said chamber provides the d.c. current necessary for electrolysing the solution to be purified, which latter is caused to flow continuously through the chamber by a pump which withdraws it from and returns it to the working vessel.

In this conventional type of apparatus the solution to be purified is free, within the cell, to move in all directions in a non-ordered manner, allowing preferential flow paths to develop which, in general, do not pass uniformly over all regions of the surface of the electrodes. Moreover, in this known apparatus the inter-electrode distances are rather large and, in any case, greater than 20 millimetres, whilst the surface areas of the two electrodes are different from one another and, largely, in the ratio of 2 to 1 (cathod to anode). Consequently, the purification of the solutions is not performed as well as it could be in that a large part of the solution can flow through the cell at a distance from the electrodes too great to allow a satisfactory electrolysis in the dwell time available.

Moreover, the different dimensions of the electrodes themselves do not permit a uniform distribution of the current in the solution and, therefor, do not allow a sufficient selectively of the purification operation.

From the GB-A-1 066 213 reference there is known an electrolytic purification apparatus substantially corresponding to the preamble of Claim 1. In this known apparatus, in particular, there are provided a plurality of anodes and cathodes arranged with a stocked arrangement in which each pair of electrodes communicate with the following pair so as to cause the solution flow exiting the first pair to enter the following pair and so on, with a Simple serpentine flow pattern.

The object of the present invention is that of eliminating the disadvantages outlined above, by providing apparatus for the electrolytic purification of solutions utilised in electro--deposition treatments and the like, which forces the solution to flow through narrow passages in such a way as to subject it uniformly to the purification treatment.

According to the present invention, this object is achieved by an apparatus for the continuous electrolytic purification of solutions utilised in electro-deposition treatment having the features of Claim 1.

A particular advantage of the apparatus of the present invention is that it can perform electrolytic purification with a uniform distribution of current within the solution to be treated so as to ensure that all parts of the solution experience substantially the same conditions.

Another advantage of the present invention is that it provides electrolytic purification apparatus which is structurally simple and of great reliability.

One embodiment of the present invention will now be more particularly described, by way of example, with reference to the accompanying drawings, in which:

Figure 1 is a side view of the embodiment; and

Figure 2 is an exploded view of a single electrode structure used in the embodiment of Figure 1.

With reference to the drawings, the elecrolytic purification apparatus forming the subject of the invention is constituted essentially by a chamber 1 resistant to acids, in which are housed assemblies of positive electrodes 2 and negative electrodes 3.

More precisely, these negative and positive electrode assemblies have an identical surface area and are counterposed and parallel to one another in such a way as to create narrow interspaces 4, at a distance from one another of between 1 and 20 millimetres, preferably between 1 and 5 millimetres, through which the solution to be purified is forced to pass by the action of a pump 5. The apparatus may be provided with its own pump or may be connected by a bypass to another pump such as the same pump already provided in the treatment apparatus for filtering the solution. The apparatus illustrated is provided with its own current rectifier 6, although it will be appreciated that this is not critical and other embodiments may draw d.c. current from another source.

In the embodiment illustrated, as shown in Figure 2, each individual purification cell, generally indicated with the reference numeral 7, is constituted by a lower bowl 8 of rectangular plan form, having an inclined floor and communicating with the outside through an elbow bend connector 9. On one of the shorter sides of this bowl, which is provided with appropriately projecting edges 10, there is coupled, by means of a double hinge 11 a cover 12 of the same outline to which is joined a duct 13 for delivering solution to be purified, which is supplied by the said pump 5. Between the edges of this bowl 8 and the cover are arranged, in series from the bottom upwardly, a first gasket 14, a first anode 2, a cathode 3 provided with transverse projections 3′, interchangeable in dependence on the distance which it is desired to create between the cathode and the anodes, a second anode 2′, and a second gasket 14′. The edges of these superimposed elements, are provided with corresponding through holes 15 in which are inserted a corresponding number of bolts 16 operable to join them all together; however opposite edges of the anode 2, the cathode 3 and the annode 2′ are spaced from the edges of the cell to define a sinuous path through the cell.

The anodes 2,2′ are preferably of insoluble type (graphite, platinised titanium, etc), although the use, in particular applications, of soluble anodes can be arranged if desired. The cathodes 3, on the other hand, are constituted by simple sheet metal pieces of steel or, of other suitable material; these are regenerable or replaceable by way of interchangeable cartridges, after a certain number of hours in service or when a certain quantity of "contaminated" deposit has accumulated thereon.

In practice, the structure, thus obtained, has close electrodes of large area between which the solution to be purified passes substantially in laminar layers, and this permits electrolysis to take place at a predeterminable and almost constant current density over all points of the surface of the cathode. Consequently, the electrolytic purification apparatus forming the subject of the invention is capable of a greater selectivity in that it makes it possible to choose the most convenient working conditions and, therefore, to establish the flow rate and accuracy of performance as a function of the type of contamination present in the solution and to be eliminated, thereby avoiding the contemporaneous and unwanted deposition of the useful metal, that is to say of the metal of which the solution is rich by its proper formulation.

Moreover, given that the whole of the solution which is pumped into the chamber 1 is constrained to flow through the narrow spaces between the anodes 2,2′ and the cathodes 3, and given that the possibility is provided of bringing the electrodes closer at will thereby obtaining a very thin laminar flow, than for a given volume of solution flowing in a given unit of time the ratio between the amount of solution present in an inter-electrode space and the layer thereof which is located facing the cathode is the lowest possible. Consequently, at any instant the quantity of depositable extraneous metallic ions as a ratio to the quantity of solution under electrolysis is the greatest possible.

The closeness of the electrodes ensures that, for the same rate of flow there is a very rapid exchange of solution in the inter--electrode spaces and a high speed of flow over the cathode. This increases the yield of deposit and, in the presence of low concentrations of contaminating ions, permits these to be extracted with the minimum possible removal of useful metal. Moreover, the energy cost to effect the desired purification treatment is reduced to the minimum. In substance, the electrolytic purification apparatus forming the subject of the invention can be utilised both for prophylactic purification (to remove the small and continuous contaminations gradually as they form) and for exceptional interventions, for example in a case in which a massive and unexpected contamination of the bath should occur. The apparatus can also function as a discontinuous purifier and is able to ensure the maximum purification with the smallest possible number of "passes".

Obviously, this apparatus, thanks to its high selectivity, is advantageously usable also for removing metallic contaminations from solutions for degreasing, pickling, activation, passivation etc used in the galvanic industry. The same apparatus, when utilised for baths which deposit alloys composed of two or more metals, permits two objectives to be achieved: first, removing a contamination caused by extraneous metal ions from those of the alloy, without compromising the concentration and the ratio of those provided for the deposition of the alloy itself; and second, re-establishing the ratio between the different ions provided for the deposition of the alloy by selectively depositing, those which are in excess. This is obtained thanks to the possibility of operating with a predetermined and very narrow range of current density, which permits the deposition predominantly of one species of metallic ions present in solution to be effected.

The present apparatus further allows the recovery of metals, particularly precious metals from exhausted solutions or from washing water; in such cases it functions, in practice, as an effluent purifier.

Claims

1. An apparatus for the continuous electrolytic purification of solutions utilised in electro-deposition treatments and the like, comprising at least a purification cell including positive and negative electrodes (2, 2′, 3) having substantially the same surface area and positioned parallel to and facing one another in such a way as to define narrow passages through which the solution to be purified is forced to pass, characterized in that said purification cell (7) is constituted by a lower bowl (8) of rectangular plan form communicating with the outside through an elbow connector (9) enabling the solution to go out, the bowl (8) having flanged edges one of which is coupled, by means of a double hinge (11) to a cover (12) having the same outline as the bowl (8), to said cover (12) there being connected a duct (13) for delivering the solution to be purified, and in that between the edges of the said bowl (8) and the cover (12) there are arranged, in series, from the bottom upwardly, a first seal (14) a first anode (2), a cathode (3) provided with transverse projections (3′) interchangeable in dependence on the distance which it is desired to set between the cathode (3) and the anodes (2, 2′), a second anode (2) and a second seal (14′).

2. A purification apparatus according to Claim 1, including at least two said cells (7) arranged in a chamber (1) resistant to acids, in which said positive (or anodes) and negative (or cathodes) electrodes (2, 2′, 3) are housed, the anodes (2, 2′) of said cells being of insoluble type such as graphite or platinised titanium, and the cathodes (3) of said cells being constituted by a material different from said anodes such as steel sheet material.

3. A purification apparatus according to any preceding Claims, characterized in that the apparatus is provided with its own pump (5) and/or its own current rectifier (6).

4. An apparatus according to claim 1, characterized in that said narrow passages are spaced from one another by a distance from 1 to 20 millimeters.

Patentansprüche

1. Vorrichtung zur kontinuierlichen elektrolytischen Reinigung von zur Elektroplattierungsbehandlungen oder dergleichen verwendeten Lösungen, mit wenigstens eine Reinigungszelle, die mit powitiven und negativen Elektroden (2, 2′, 3) vorgesehen ist, die wesentlich dieselbe Fläche weisen auf und parallel aneinandergegenüber angeordnet sind, um so enge Durchgänge zum erzwungen Durchgang der zu reinigenden Lösung zu bestimmen, dadurch gekennzeichnet, dass die obengenannte Reinigungszelle (7) aus einer eben rechtwinkeligen Unterschale (8) besteht, die durch einen die Lösung auslassende Bogen (9) mit Aussen in Verbindung steht, wobei die Schale (8) mit angeflanschten Rändern vorgesehen ist, deren einen mittels eine Doppelscharniere (11) mit einem dasselbe Profil der Schale (8) aufweisenden Deckel (12) gekoppelt ist, wobei dem obengenannten Deckel (12) ein Kanal (13) zum Durchgehen der zu reinigenden Lösung gekoppelt ist, und dass zwischen den Rändern der obengenannten Schale (8) und dem Deckel (12), in Folge, von oben bin unten, ein erster Siegel (14), eine erste Anode (2), eine Kathode (3), die mit gemäss dem zu bestimmenden Abstand zwischen der Kathode (3) und der Anoden (2, 2′) auswechselbaren Quervorsprungen (3′) vorgesehen ist, eine zweite Anode (2) und ein zweiter Siegel (14) vorgesehen sind.

2. Reinigungsvorrichtung nach Anspruch 1, wo wenigstens zwei der obengenannten Zellen (7) in einer die obengenannten positiven Elektroden (oder Anoden) und negativen Elektroden (oder Kathoden) (2, 24, 3) aufnehmenden säurebeständigen Kammer (1) angeordnet sind, wobei die Anoden (2, 2′) der obengenannten Zellen unlösartig als der Graphit oder der platinierte Titanium sind, und die Kathoden (3) der obengenannten Zellen aus einem Material verschiedend der obengenannten Anoden, als stahlblättiger Material, bestehen.

3. Reinigungsvorrichtung nach irgendeinem vorhergehendem Anspruch, dadurch gekennzeichnet, dass die obegenannte Vorrichtung mit einer eigenen Pumpe (5) und/oder einem eigenen Stromrektifikator (6) vorgesehen ist.

4. Reinigungsvorrichtung nach Anspruch 1, dadurch gekennzeichnet, dass die obengenannten engen Durchgänge mit einem Abstand von 1 bis 20 Millimetern aneinander getrennt sind.

Revendications

1. Appareillage pour la purification en continu électrolytique de solutions employées dans les traitements d'électro-dépôt et similaires, comprenant au moins une cellule de purification contenant électrodes positives et négatives (2, 2′, 3) présentant essentiellement la même surface et étant arrangées parallèlement l'une de face à l'autre de façon de définir des passages étroits à travers lesquels la solution à être purifiée est forcée de passer, caractérisé en ce que ladite cellule de purification (7)se forme d'un bassin inférieur (8) ayan une forme plaine ractangulaire, communiquant avec l'extérieur à travers d'un raccord coudé (9) qui permet à la solution de sortir, le bassin

(8) présentant des bords emboutis l'un desquels est accouplé au moyens d'une charnière double (11) à un couvercle (12) présentant le même profil du bassin (8), audit couvercle (12) il y étant joint une conduite (13) pour amener la solution à être purifiée; et en ce que entre les bords dudit bassin (8) et le couvercle (12) il y a arrangé, en série, du haut en bas, un premier cachet (14), une première anode (2), une cathode (3) munie de saillies transversales (3′) interchangeables selon l'écart qu'on veut établir entre la cathode (3) et les anodes (2, 2′), une deuxième anode (2) et un deuxième cachet (14′).

2. Appareillage de purification selon la revendication 1, contenant au moins deux desdites cellules (7) arrangées dans une chambre (1) résistante aux acides, où lesdites électrodes positives (ou anodes) et négatives (ou cathodes) (2, 2′, 3) sont logées, les anodes (2, 2′) desdites cellules étant du type insoluble, comme la graphite ou le titanium platiné, et les cathodes (3) desdites cellules étant formées par un matériel différent desdites anodes, comme un matériel en feuilles d'acier.

3. Appareillage de purification selon l'une quelconque des revendications précédentes, caractérisé en ce que ledit appareillage est muni d'une pompe (5) à soi et/ou d'un rectifieur de courant (6).

4. Appareillage selon la revendication 1, caractérisé en ce que lesdits passages étroits sont écartés les uns les autres d'un écart de 1 a 20 mm.

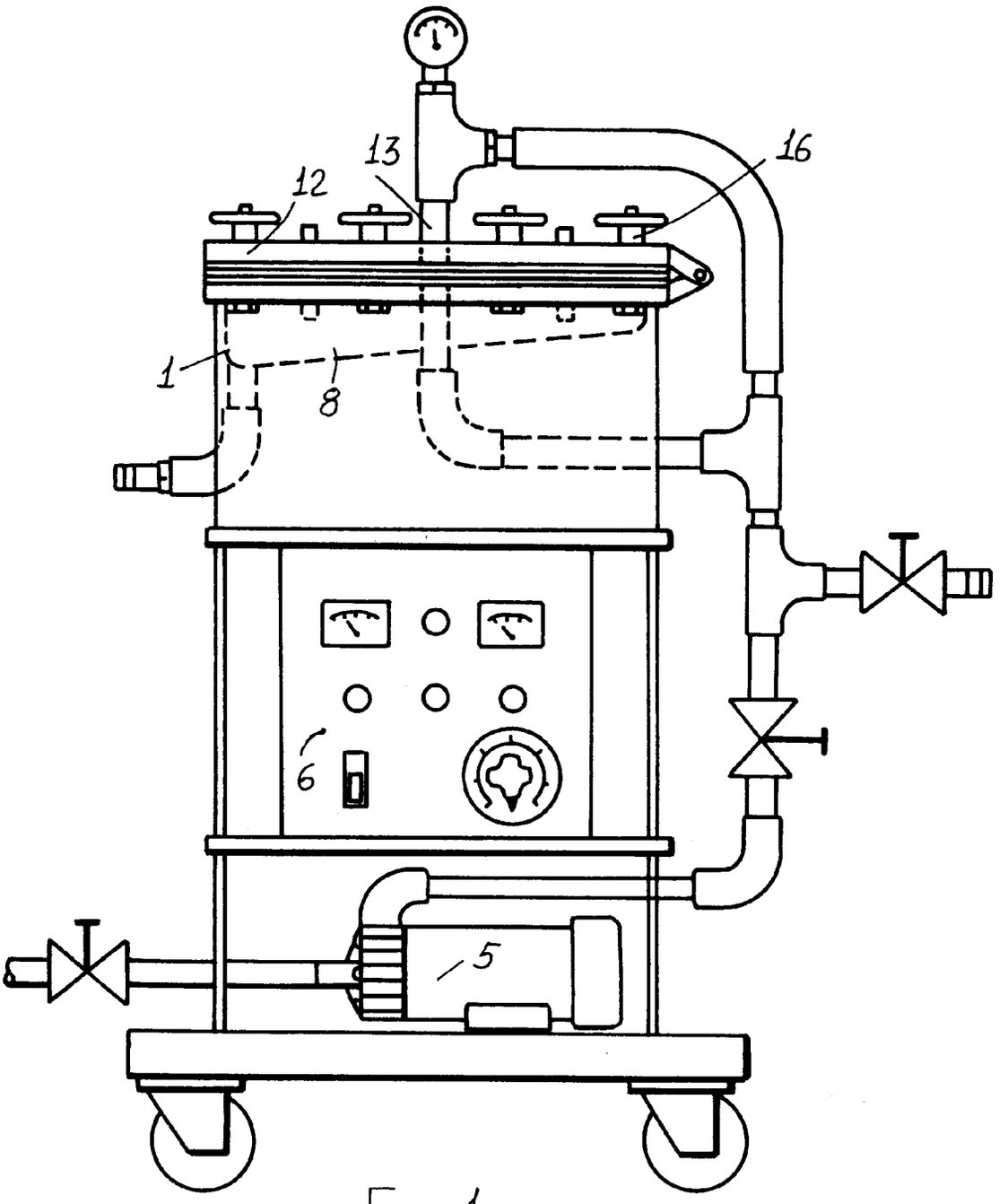

FIG. 1

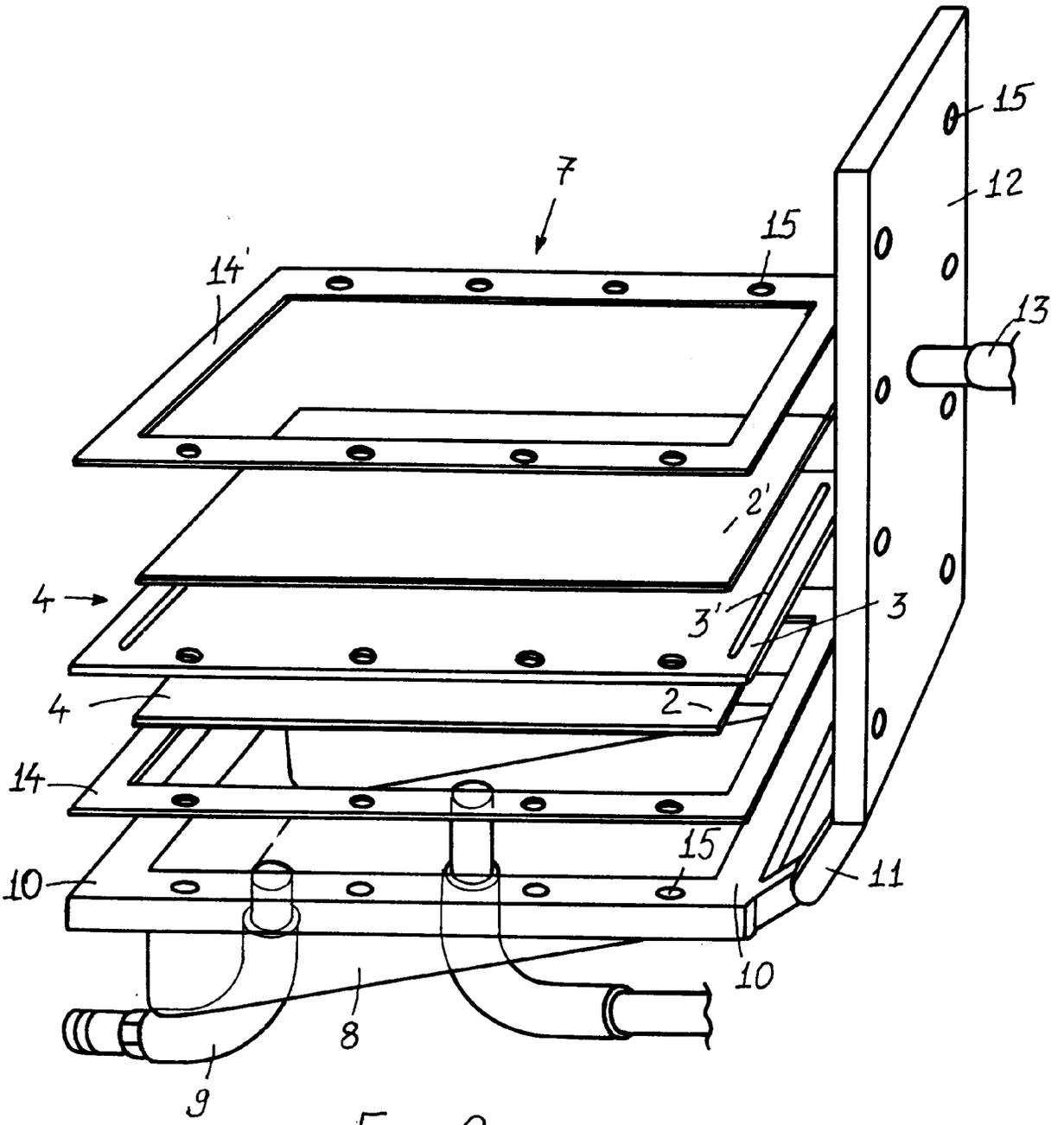

FIG. 2