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(54) A corrosion-resisting electrolytic cell.

(57) A corrosion-resisting electrolytic cell equipped with a cation exchange membrane is disclosed. An iron cathode and an iron cathode structure are treated with alkali-proof coating excepting portions which are in contact with catholyte and are 30 mm, at the most, apart in the shortest distance through liquid from the nearest portion of an anode. The invention eliminates the problems caused by iron ion dissolved including a decrease in quality of the product and deterioration of the cation exchange membrane.

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A CORROSION-RESISTING ELECTROLYTIC CELL

BACKGROUND OF THE INVENTION

The present invention relates to a cathode structure of an electrolytic cell equipped with a cation exchange membrane, more particularly to an improvement in corrosion resistance and durability of an iron cathode structure.

The electrolysis of an aqueous alkali metal halide solution has been carried out by a mercury process electrolytic cell or an asbestos diaphragm process electrolytic cell, but, recently an electrolytic cell providing a cation exchange membrane has been put into practice. Such electrolytic cells for the electrolysis of an aqueous alkali metal halide solution to produce an alkali metal hydroxide liquor normally employ mild steel as a material of a cathode and a cathode structure which are in contact with an alkali metal hydroxide liquor. Mild steel possesses sufficient strength as a structure material, superior processability and is cheap, and is therefore the most suitable material as the cathode structure. Moreover, when used as a cathode it has a remarkable feature of relatively low hydrogen overvoltage.

Electrolytic cells providing cation exchange membranes are normally operated with a concentration of the catholyte being 15 % or more, moreover, 20 % or more. Furthermore, in the case of a cation exchange membrane whose ion exchange groups are, partly or wholly, carboxylic

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acid groups, operation is effected with the catholyte of 30 % or more. When the operation is made with the catholyte having such a high concentration, dissolution of mild steel takes place to thus increase the content of iron ion in the catholyte. That is, the content of iron ion in an alkali metal hydroxide solution, the product, increases and the quality of the product is thus degraded. The higher the electrolytic temperature becomes, the more prominent the tendency is. In addition, deposition of iron ion onto the cation exchange membrane increases to invite the deterioration of the membrane. Moreover iron ion dissolved into the catholyte is reduced to deposit on the surface of the cathode close to an anode. Accordingly, in this situation it is impossible to raise the electrolysis temperature to suppress the dissolution of iron as low as possible and hence operation at high cell voltage is unavoidable.

In order to avoid these defects of mild steel, the cathode structure is rebuilt anew with an expensive material such as nickel or high chrome steel but the process is not advantageous because of costly materials and processing leading to an increase in equipment cost.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a corrosion-resisting electrolytic cell at a low cost.

It is another object of the present invention to provide an electrolytic cell free of problems caused by

iron ion dissolved including such as a decrease in quality of the product and deterioration of a cation exchange membrane.

These and other objects of the present invention together with the advantages thereof will become apparent to those skilled in the art from the detailed disclosure of the present invention as set forth hereinbelow.

Through a series of studies, the present invention has been completed based on the discovery that the foregoing objects can be achieved by treating with alkali-proof coating an iron cathode structure, excepting portions which are in contact with catholyte and are 30 mm, at the most, apart in the shortest distance through liquid from the nearest portion of an anode.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a curve showing the relation between the concentration at which a cathodic iron material dissolves and corrodes and the shortest distance liquid from the nearest portion of an anode to a cathode structure.

FIG. 2 is a top plan view illustrating an embodiment of the cathode structure of an apparatus of the present invention and FIG. 3 is a cross-sectional view taken in the direction of the arrows along the A-A' line in FIG. 2.

FIG. 4 is a cross-sectional view taken in the direction of the arrows along the B-B' line in FIG. 2, showing an embodiment of a corrosion-resisting process.

FIG. 5 is a partial cross-sectional view illustrating an embodiment in which a cation exchange

membrane is positioned to an electrolytic cell of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is to provide a corrosion-resisting electrolytic cell which is characterized in that in an electrolytic cell equipped with a cation exchange membrane for the electrolysis of an aqueous alkali metal halide solution to produce an aqueous alkali metal hydroxide liquor having the concentration of 15 % or more, an iron cathode structure is subjected to alkali-proof coating, excepting portions which are in contact with catholyte and are 30 mm, at the most, apart in the shortest distance through liquid from the nearest portion of an anode.

The present invention is applicable to any type of cation exchange membrane electrolytic cell, especially to finger type electrolytic cells advantageously.

The finger type electrolytic cell herein used may not only involve a finger type construction cell such as described at page 93, CHROLINE-Its Manufacture, Properties and Uses, edited by J. S. Sconce, issued by Reinhold Publishing Corporation, New York, 1962, but a flattened tube type construction cell.

An iron cathode taking part in a cathode reaction is cathodically polarized and electrically anticorrosive but an iron cathode and an iron cathode structure not taking part in the cathode reaction are insufficient in cathodic polarization to thus come to be in the corrosive region, and

the dissolution of iron into catholyte increases. A finger type cell, in particular, is generally complicated in its inside construction of the cathode, involving many portions insufficient in cathodic polarization and thus the content of iron ion increases in the catholyte. The research on the relation between the portions insufficient in cathodic polarization and the content of dissolved iron ion was made and the obtained results are given in FIG. 1. FIG. 1 is a curve in which the concentrations of the catholyte were plotted which exhibit zero decreasing points at 80°C at various portions different in the shortest distance through liquid from the anode.

The zero decreasing point herein means a boundary point at the distance; in cases where nearer to the anode the portions cause Fe ion in the catholyte to reduce and deposit thereon, in cases where farther from the anode those invite the dissolution and loss of iron.

Meanwhile, the finger type cell has a merit that it was originally developed to be served for an asbestos diaphragm electrolysis process at a low manufacture cost and facilitates the scale-up of the manufacturing equipment. In the operation of a finger type cell providing an asbestos diaphragm, the catholyte normally has the concentration ranging from 11 to 13 %. In such the concentration, most of the cathode structure belong to the anticorrosive region, as apparent from FIG. 1, and even though in the corrosive region, the corrosion speed is slow and accordingly the

concentration of iron ion contained in the catholyte is kept at a low level. Moreover even when iron deposits on the asbestos diaphragm, no great deterioration of the diaphragm occurs.

On the other hand, when a finger type cell providing a cation exchange membrane is operated, the concentration of the catholyte normally exceeds 15 %, occasionally 30 %. Therefore, as clear from FIG. 1, the corrosive region extends and the dissolved amount of iron increases. As a result, a decrease in the quality of the product as well as deterioration of the membrane owing to the deposited iron is brought about.

For instance, when the operation is effected with the catholyte concentration of 30 %, it is understood from FIG. 1 that iron starts to dissolve at the shortest distance through liquid from the anode of approximately 30 mm. Accordingly, taking it into consideration that the operation is carried out with the catholyte concentration of 30 % or more, it is necessary to treat with alkali-proof coating portions of the cathode and the cathode structure which are farther than 30 mm, more preferably farther than 20 mm, most preferably farther than 10 mm from the anode, to put it another way, the cathode and the cathode structure excepting portions within 10 mm. In the case of the catholyte concentration being 15 % or below, it is understood that most surfaces of the cathode structure are in the anticorrosive region.

The corrosion resistance is afforded by alkali-proof coating using known or conventional arts but, in the case of complicated structures, nonelectrode plating (chemical plating) with nickel is especially effective. Besides, alkali-proof coating such as electroplating, plasma flame spray with nickel, rubber-lining and the like may also be employed.

The alkali-proof coating in the apparatus of the present invention may be also applied to filter-press type cells with a view to corrosion resistance of back plates of cells, cell liquor removal pipes and the like which are great in the shortest distance through liquid from anodes.

According to the present invention, it is not necessary to corrosion-proof coat the entire surface of iron cathodes and an iron cathode structure but well to perform partial corrosion-proof coating and thus electrolytic cells which are superior in durability and produce an aqueous alkali metal hydroxide liquor with high concentration and high purity can be provided at very low cost.

Moreover, the dissolution of iron from an iron cathode structure is effectively prevented and thus the electrolytic temperature can be raised. Therefore, a decrease in cell voltage owing to an increase in electrolytic temperature is resulted.

Furthermore, alkali-proof coating of the entire surfaces of the iron cathode invites problems including an increase in hydrogen overvoltage and an undesired increase

in cell voltage and is thus not desired.

As a cation exchange membrane used in the apparatus of the present invention, perfluorocarbon membranes having ion exchange groups such as carboxylic acids, sulfonic acids and sulfonamids are used, an example of which is sold under the trademark "NAFION" by E. I. Du Pont de Nemours & Company. These ion exchange groups are used singly, in combination or in a layered structure.

Hereinafter an embodiment of the present invention will be explained in more detail referring to FIG. 2 and FIG. 3.

FIG. 2 is a top plan view showing a finger type electrolytic cell used in an example and FIG. 3 is a cross-sectional view taken in the direction of the arrows along A-A' line in FIG. 2.

In these drawings, a cathode box of a finger type electrolytic cell is surrounded by side walls 1 and possesses opened portions 4, each of which is surrounded by perforated steel plates 6.

The perforated steel plates 6 are connected to perforated steel plates 2 welded to inner edges of flanges 5.

Accordingly, it is vertical steel plates 6 in opposition to anodes inserted into the opened portions 4 that act as cathodes.

In FIG. 4, on the upper and lower flanged portions 5, covers are put which are equipped with an inlet 10 for circulating a plating solution and an outlet 11

capable of adjusting the level of the plating solution, respectively, and nonelectrode plating with nickel is applied to four surfaces divided by C-C', D-D', E-E' and F-F' shown in FIG. 3 and FIG. 4, with the cathode structure set up vertically.

That is, the level of the plating bath is controlled so that the backside 12 of the outermost perforated steel plate, the perforated steel plate 2 connected to the flanges and the inside surface 13 of the side walls are plated.

Hereinbelow, explanation will be made as to an experiment using an electrolytic cell of the present invention.

EXPERIMENT

Plating was applied to the electrolytic cell shown in FIG. 2 to FIG. 4 at 90° C for 2 hours using "TOPNICOLON-N-47" produced by OKUNO CHEMICAL INDUSTRY COMPANY LIMITED and controlling the concentration of nickel ion to 5 - 6 g/l. The thickness of the plated layer was 30 μm on an average. The plated portions of the cathode structure were 15 mm or more apart in the shortest distance through liquid from the nearest portions of anodes.

To this cell a perfluorocarbon cation exchange membrane was positioned which had carboxylic acid groups to the cathode side and sulfonic acid groups to the anode side.

In FIG. 5 there was shown a partial cross-sectional view of the finger type electrolytic cell providing the cation exchange membrane.

The anode 14 was inserted into the opened portion 4 and the cation exchange membrane 18 was positioned by the use of cation exchange membrane supporting devices 16. The supporting device was made of corrosion-resistant plastics or corrosion-resistant metals.

Using the electrolytic cell, electrolysis was carried out under the following conditions;

NaCl concentration of anolyte	3.5 N
Caustic soda concentration of catholyte	30 %
Electrolytic temperature	90° C
Current density	23.5 A/dm ²

Electrolytic voltage was 3.5 volts. The concentrations of iron ion and nickel ion contained in the catholyte were 0.2 ppm and 0.03 ppm, respectively. After the continuous operation for one month, almost no ion deposited onto the cation exchange membrane was observed.

For comparison, experiment was performed under similar conditions excepting that a nonplated electrolytic cell was employed. In the catholyte 0.4 ppm of iron ion and 0.01 ppm of nickel ion were contained and cell voltage was 3.5 volts. After one-week operation, the cation exchange membrane was discolored to brown.

For further comparison, using an electrolytic cell, the whole of the cathode structure of which was plated under the same plating conditions as aforesaid, operation was conducted. Cell voltage amounting to 3.7 volts was necessitated.

WHAT WE CLAIM IS:

1. In an electrolytic cell providing a cation exchange membrane for electrolysing an aqueous alkali metal halide solution to obtain an aqueous alkali metal hydroxide liquor with a concentration of 15 % or more, the improvement of which comprises alkali-proof coating an iron cathode structure, excepting portions which are in contact with catholyte and are 30 mm, at the most, apart in the shortest distance through liquid from the nearest portion of an anode.

2. The electrolytic cell of Claim 1, wherein said portions excepted are 20 mm, at the most, apart in the shortest distance through liquid,.

3. The electrolytic cell of Claim 1, wherein said portions excepted are 10 mm, at the most, apart in the shortest distance through liquid.

4. The electrolytic cell of Claim 1, wherein said iron cathode structure is of a finger type.

5. The electrolytic cell of any of preceding claims, wherein said alkali-proof coating is nonelectrode plating with nickel.

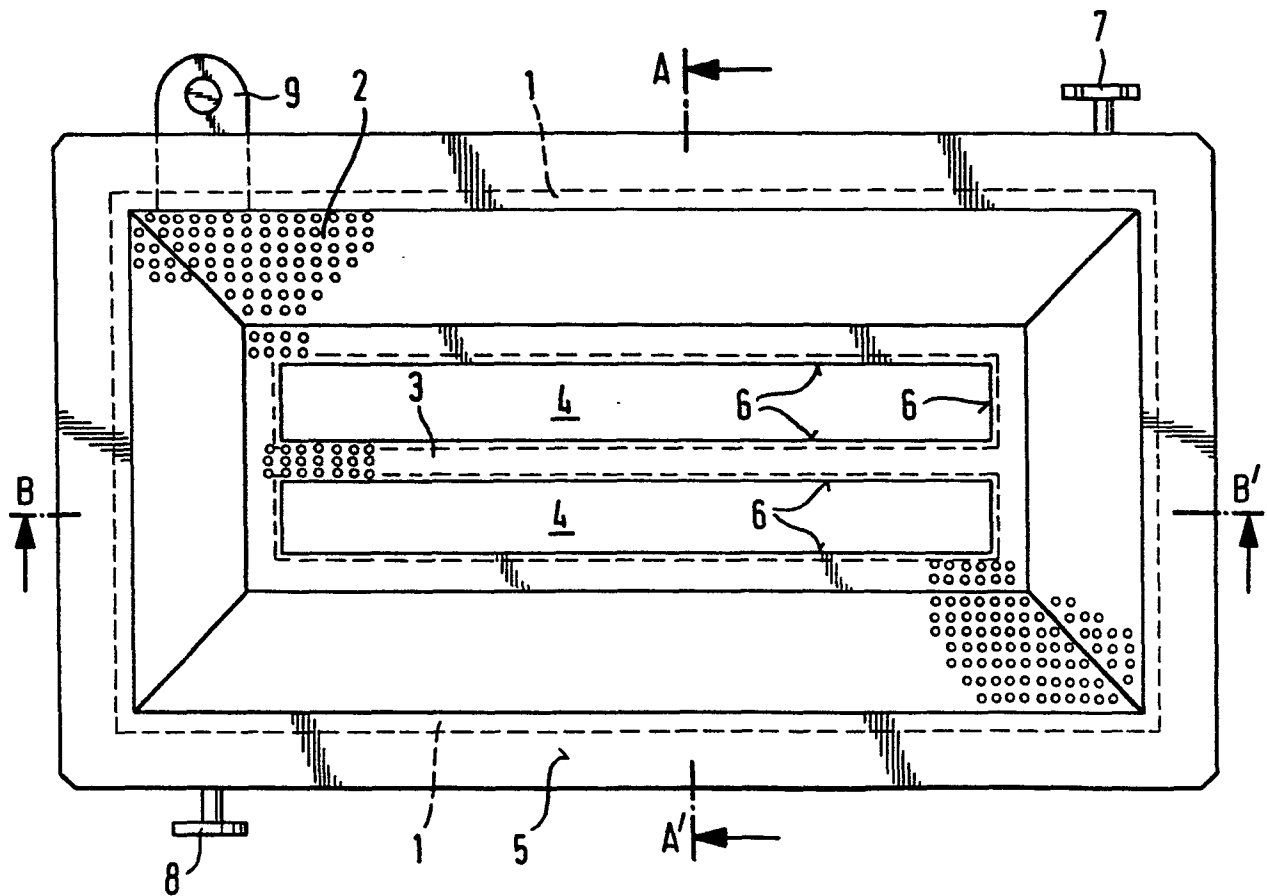
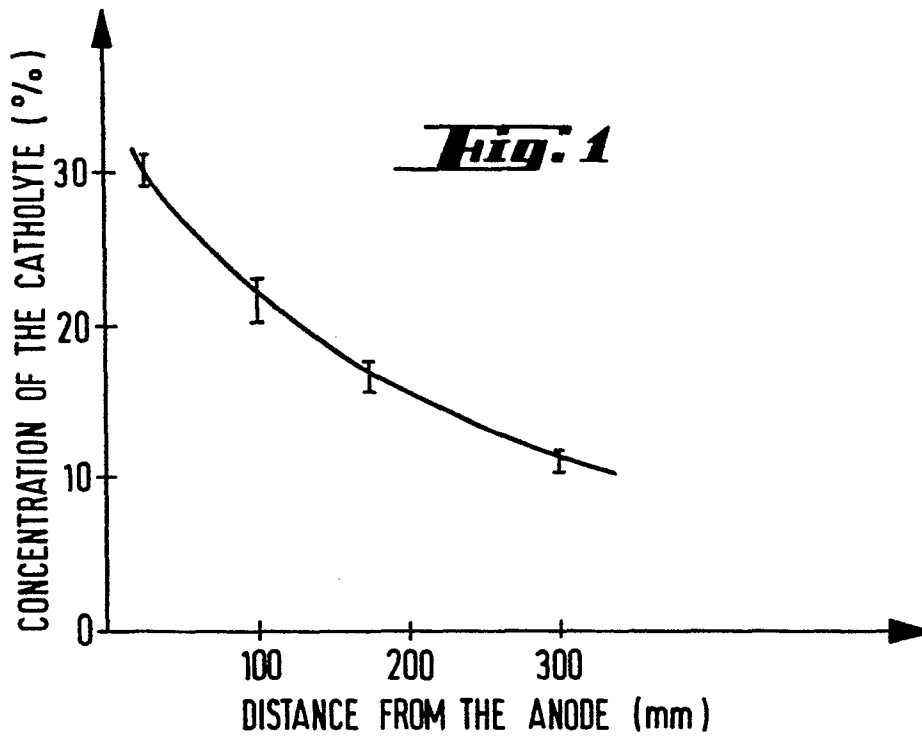


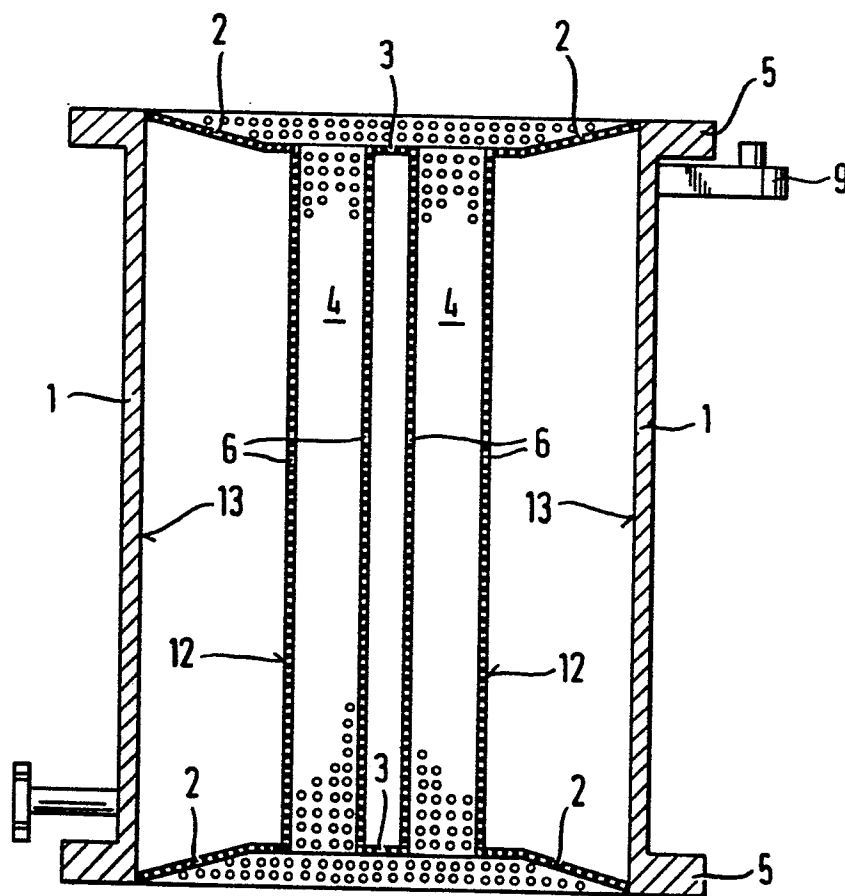
Fig. 3 (A-A')

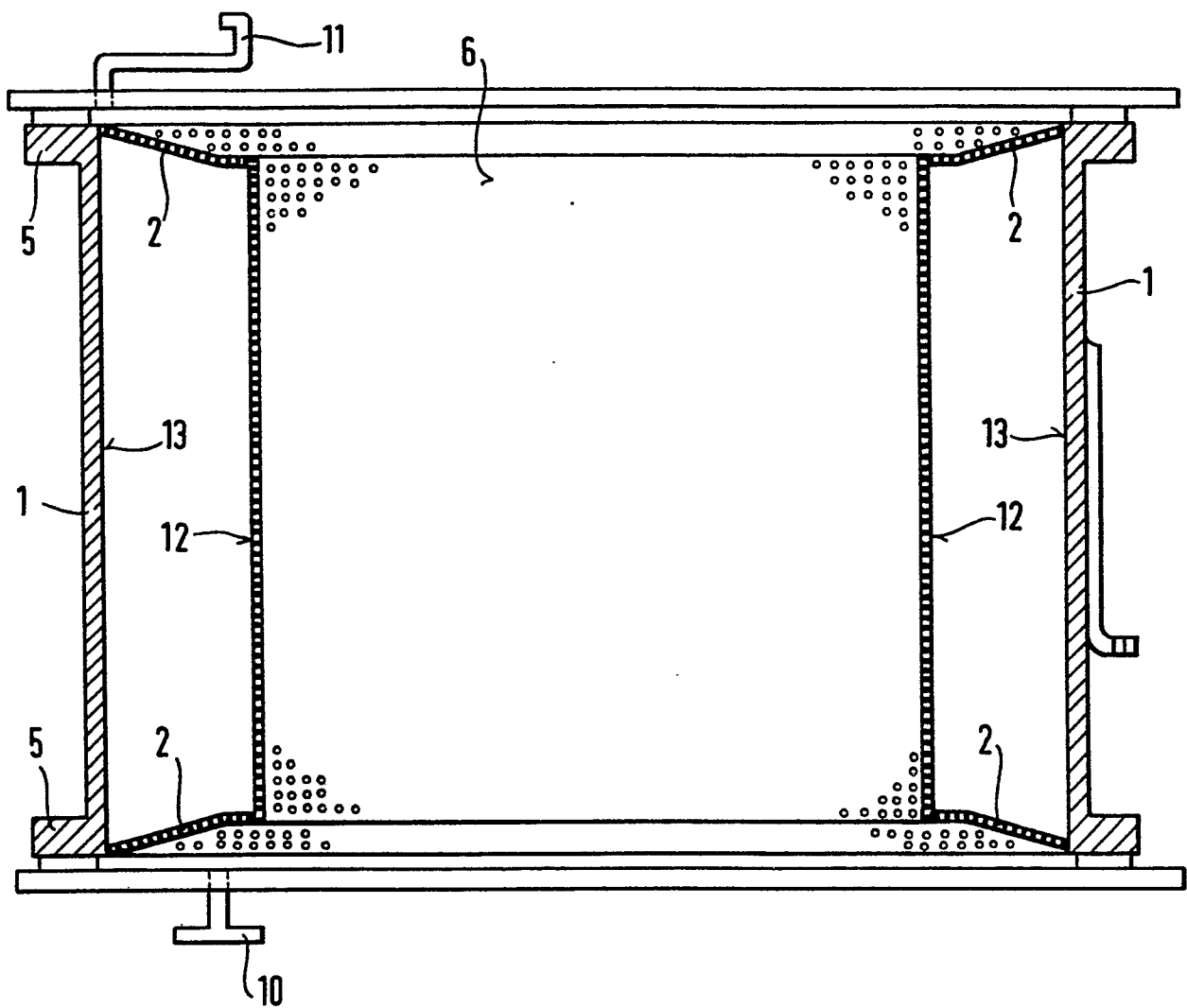
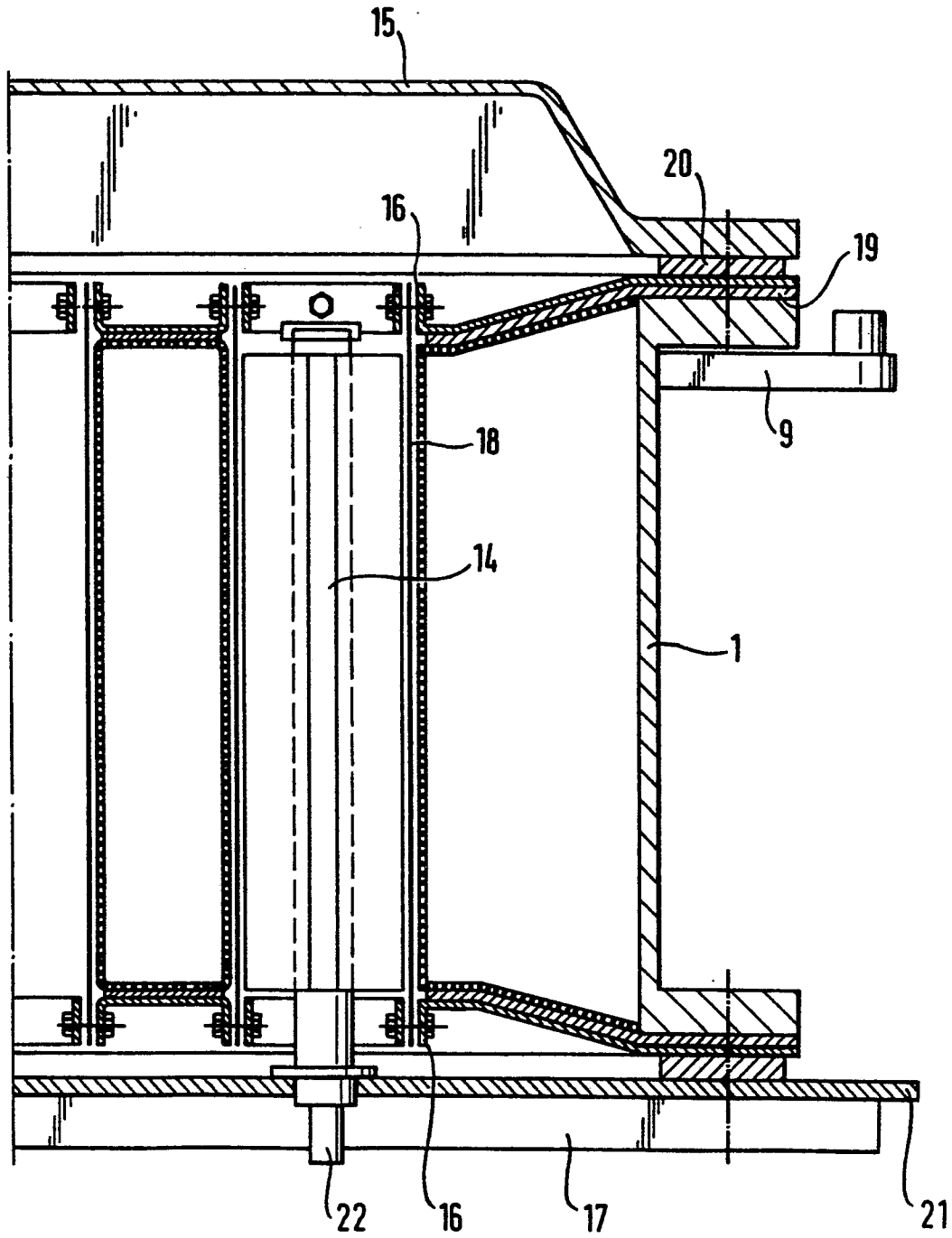
Fig. 4 (B-B')

Fig. 5



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EUROPEAN SEARCH REPORT

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Application number

EP 83 10 0948

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X,Y	EP-A-0 031 948 (ASAHI KASEI KOGYO KABUSHIKI KAISHA) *Page 10, line 1 - page 13, line 28; page 20, line 9 - page 21, line 6; claims*	1-5	C 25 B 11/04
Y	EP-A-0 034 408 (PERMELEC ELECTRODE LTD) *Page 4, lines 1-17; page 5, lines 19-22; claims*	1-5	
Y	EP-A-0 015 057 (MPD TECHNOLOGY) *Claims*	1,5	
A	NL-A-7 701 589 (BASF WYANDOTTE)		
A	FR-A-2 384 036 (TOKUYAMA SODA KABUSHIKI KAISHA)		
A	DE-A- 462 302 (ANSCHÜTZ & CO.) *Page 2, lines 14-19*		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 26-04-1983	Examiner GRUNDKE H.H.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			