



(19)

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(11)

EP 0 722 000 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
17.07.1996 Bulletin 1996/29

(51) Int. Cl.⁶: **C23F 13/02**

(21) Application number: **96610001.8**

(22) Date of filing: **10.01.1996**

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

(72) Inventor: **Nielsen, Jan S.**
DK-2620 Albertslund (DK)

(30) Priority: **13.01.1995 DK 35/95**

(74) Representative: **Simonsen, Christian Rosendal et al**
c/o Internationalt Patent-Bureau
Hoeje Taastrup Boulevard 23
DK-2630 Taastrup (DK)

(71) Applicant: **DANSK ELEKTROLYSE A/S**
2620 Albertslund (DK)

(54) Apparatus for corrosion protection of a water system

(57) An apparatus for corrosion protection of a water system is disclosed, where a hitherto unknown principle for the production of ions of alkaline sensitive metal is used. The apparatus comprises a container (1,14,17), fully or partly flown through by the water, connected as cathode and/or comprising at least one cathode (9,10), the apparatus being provided with at least one anode (3), wherein cathode and anode are connected to a DC

source, characterized in that at least one electrode (4), comprising alkaline sensitive metal and electrically isolated from the cathode and the anode connected with the DC source, is provided such that at least a part of the electrical current running through the water from the anode to the cathode, is forced through the electrode comprising alkaline sensitive metal.

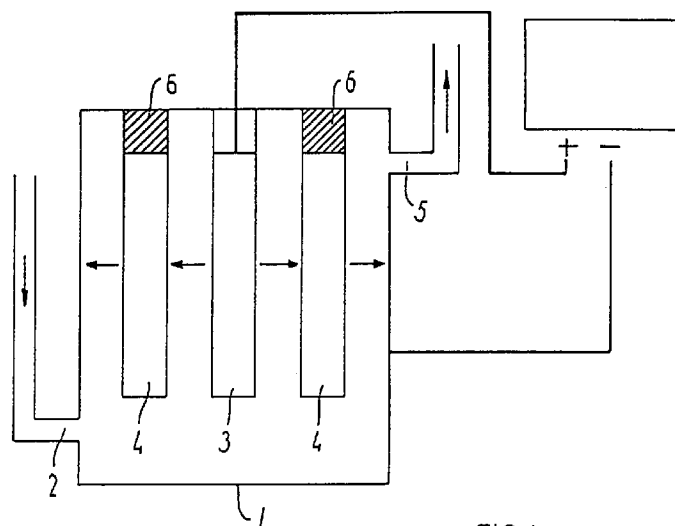


FIG.1

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Description

The present invention relates to an apparatus for corrosion protection of a water system, for example a hot water system, a radiator system or a process water system.

It is usual to corrosion protect for example a container or other elements in a water system by applying a negative voltage to the container and a positive voltage to an electrode present in the container. This form of protection is generally described as cathodic protection. However, cathodic protection has the drawback that the protecting effect only extends to a relatively small area around the electrode connected as an anode, which results in that the following piping system is not protected against corrosion.

In this known form of protection it is possible to use several anodes to protect larger areas, but regarding large systems with large pipings it is not practical to provide the whole piping system with a large number of anodes, and therefore there has been an interest in finding other methods to corrosion protect.

Such a method comprises the use of an electrolysis system, i.e. a system, where the anode material is of an alkaline sensitive metal, like aluminium. In the cases where the alkaline sensitive metal is aluminium, it will dissolve by electrolysis as the aluminium ion Al^{3+} in the acid environment around the anode.

The aluminium ions formed by the electrolysis will convert, influenced by hydroxide formed by the cathode, to negative aluminate ions (AlO_2^- or $Al(OH)_4^-$), due to the fact that the pH-value of the consumption water normally is in the weak basic area between pH 7,5 and pH 8,5. In connection with this conversion the aluminium ions have to pass an isoelectric point around pH 6. At this isoelectric point aluminium has a low solubility and it is presumed that the large observed deposit of sediment by electrolysis is due to precipitation of aluminium. Besides that the siltation in itself is undesirable, because it provides good conditions for growth of micro organisms, the deposit of silt also means that there is less aluminium, dissolved from the anode, available for corrosion protection of the water system. Furthermore, if the container comprise a heating element, deposit on the heating element will cause a poor heat transmission from the heating element to the water in the container. Consequently, it is necessary frequently to clean the container.

It has also been suggested to connect an aluminium electrode as cathode, see Danish patent specification no. 167870 B1. Hereby the negative aluminium comprising ion AlO_2^- is formed in the aqueous environment around the cathode.

The present invention provides a hitherto unknown principle for production of ions of alkaline sensitive metal, wherein the alkaline sensitive metal is connected neither as anode nor as cathode, as disclosed in the prior art.

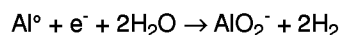
The object of the present invention is to provide an apparatus for corrosion protection of a water system with less formation of silt, said corrosion protection being

more effective than for a conventional cathodic protection system or an electrolysis system.

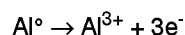
This is obtained according to the invention by an apparatus for corrosion protection of a water system, comprising a container, fully or partly flown through by water, connected as cathode and/or comprising at least one cathode, the apparatus being provided with at least one anode, wherein cathode and anode are connected to a direct current (DC) source, which apparatus is characterized in that at least one electrode, comprising alkaline sensitive metal and electrically isolated from the cathode and the anode connected to the DC source, is provided such that at least a part of the electric current, running in the water from the anode to the cathode, is forced through the electrode comprising alkaline sensitive metal.

Not limiting the present invention to any special theoretical explanation, it is assumed that ions of alkaline sensitive metal are produced in the following way for a system, where an electrode comprising alkaline sensitive metal is placed between an anode and a cathode:

The side of the electrode comprising alkaline sensitive metal, facing the current running from the anode, will receive electrons. This will cause that there on this side will be a cathode reduction of the alkaline sensitive metal. As the skilled person knows that every alkaline sensitive metal may be used in the present invention, the invention will in the following be exemplified with aluminium. The cathode reduction for aluminium is assumed to follow the following reaction equation:



On the side of the electrode comprising alkaline sensitive metal facing the cathode, electrons will be released to the cathode. It is assumed that the dissolution of aluminium follows the following reaction equation:



As shown in the above equations, theoretically three times more AlO_2^- than Al^{3+} are produced per coulomb, which might explain the fact that there from the side facing the anode is dissolved the most alkaline sensitive metal, and that there from the side facing the cathode is dissolved a smaller amount. This predominant production of aluminate results in a smaller siltation and an efficient corrosion protection of the following water system.

The terms "anode" and "cathode" refer to electrodes connected as anode and cathode, respectively, i.e. connected to the positive and negative pole, respectively, on the DC source. These electrodes may both be of a permanent and/or a soluble type. As a permanent electrode may be used an electrode comprising magnetite, platinized titanium, iron or graphite. As a soluble electrode is preferred an electrode comprising one or more alkaline sensitive metals selected from aluminium, zinc, tin or lead, aluminium being preferred. Especially a permanent electrode is used as an anode.

The electrode comprising alkaline sensitive metal is selected such, that it comprises aluminium, zinc, tin, lead or mixtures thereof, preferably aluminium.

As the container, which is connected as cathode and/or which comprises at least one cathode, such may be used, which is installed as a partial or a full stream container in the water system, or a container which of other reasons is installed in the water system, for example a hot water container or a pressure tank. The container may be of any suitable material, especially metal or metal alloys, for example metal material comprising iron. If the container is of a material, or the container is fully coated with a material, which is not electrical conducting, the container obligatory comprises one or more cathodes. In the present description and claims, when the container is connected as a cathode, is also meant, besides the container flown through by water, arrangements in the container electrically connected with the container, and thereby having the same potential.

The at least one anode, provided in the apparatus, may be present in the same container as the container connected as cathode and/or comprising at least one cathode, but the anode may also be present in a separate container, or in a separate chamber, which maybe is in liquid communication with the first mentioned container.

In such case where the anode is present in the same container connected as cathode and/or comprising at least one cathode, electrical isolated alkaline sensitive metal may be placed between cathode and anode. Hereby ensuring that the current running from anode to cathode is forced through the alkaline sensitive metal.

To control and concentrate the direction of the current it may be desirable fully or partly to coat the inner walls of the container with an electrically isolating material. Alternatively the walls of the container may fully or partly be constituted of an electrically isolating material. Preferably this electrically isolating material is provided in areas, where an electrically isolating alkaline sensitive metal is not placed between the at least one anode and a container wall used as cathode.

Even though good results are obtained with the above mentioned embodiment, a better control of the electrical currents running in the water may still be desirable. A better control ensures partly a more predictable result, partly less current loss.

A way to obtain a better control of the currents is to separate the at least one anode from the at least one cathode present in the same container by providing two chambers, which might be in liquid communication. This may for example be provided by partition in the container separating anodes from cathodes. Hereby a first chamber comprises at least one cathode and at least one electrode, isolated from the cathode, which might comprise alkaline sensitive metal, and a second chamber comprises at least one anode and at least one electrode, isolated from the anode, comprising alkaline sensitive metal, the electrodes isolated from anode and cathode in the two chambers being connected, thereby obtaining the same potential.

Another way to obtain a better control of the currents, is to separate the at least one anode from the at least one cathode in separate containers. Hereby a first container is connected as cathode and/or comprises at least one cathode and comprises at least one electrode electrically isolated from the cathode, and a second container comprises at least one anode and at least one electrode electrically isolated from the anode, comprising alkaline sensitive metal, the electrodes isolated from anode and cathode in the two containers being connected, thereby obtaining the same potential.

By separating anodes and cathodes in separate chambers in the same container or in separate containers, practically a complete control of the electrical currents running in the water can be obtained. In addition to this, it is possible directly to measure the electrical current running between the electrodes isolated from cathode and anode in the two chambers, by inserting an amperemeter in the electrical connection between the electrodes. The measured current is a direct expression for the amount of dissolved alkaline sensitive metal and it is therefore possible to control the formation of ions of alkaline sensitive metal by changing the amount of current supplied to anode and cathode from the DC source, so that the corrosion protection at any time can operate optimally, even under changed conditions, such as a changed amount of flowing water in the water system, a changed water temperature, a changed pH-value of the water, etc.

An essential advantage by using an apparatus according to the invention with separate chambers or containers, is that different ions of alkaline sensitive metal in the two chambers/containers are formed, when electrodes of alkaline sensitive metal isolated from cathode and anode, are used in both containers. In the chamber/container comprising the at least one cathode the positive ion is produced, and in the chamber/container comprising the at least one anode the negative ion is produced. If, for example, only the negative ion is desired, one may omit to connect the chamber/container comprising the cathode to the same water system as the chamber/container comprising the anode. Alternatively, there may be provided a permanent electrode in the chamber/container comprising the cathode, which permanent electrode is isolated from the cathode but is connected to the electrode comprising alkaline sensitive metal in the chamber/container comprising the at least one anode. If aluminium is used as alkaline sensitive metal, then it is possible to supply the water system with the desired aluminate ion.

If two containers are used, comprising anode and cathode, respectively, the inner walls of these containers, to avoid corrosion and influence on the electrochemical processes, are preferably coated with, or the containers mainly consists of, electrical isolating material. In these containers the cathode and the anode, respectively, may favourably be placed close to or embedded in the wall of electrical isolating material and the electrodes isolated from cathode and anode may be provided in the centre

of the container with free liquid flow to all sides. Hereby it is ensured, that the majority of the water flowing through the container, passes between the isolated electrodes and cathode/anode, such that a uniform distribution of ions of alkaline sensitive metal in the water is obtained, and such that good water flow conditions appear in the containers.

It is preferable to install the apparatus according to the invention such in the water system that a constant part of the full flow passes through the apparatus. This is, in general, ensured by connecting a feeding pump, which supply a constant flow rate. If desired, the amount of current, which is supplied to the anodes and the cathodes, is adjusted dependent on the full flow, so that ions of alkaline sensitive metal are released in dependence on the consumed amount of water.

After some use of the apparatus according to the invention, a formation of coating on the electrodes, especially the cathode, may be observed. This coating may prevent an effective use of the apparatus and is therefore undesirable. Surprisingly, it has been proven, that this coating can be avoided, or even removed, if the apparatus is operated with alternating polarity, so that the electrodes functioning as anode and as cathode, respectively, in one time period changes polarity to cathode and anode, respectively, in another time period. The length of the periods, in which an electrode is cathode or anode, is adjusted according to the desired result. If desired, alternating current may be used.

As there, as previously mentioned mainly is observed formation of coating on the cathode, one may, to obtain a more effective cleaning of the cathode, apply a positive potential to the electrodes isolated from cathode and anode. Hereby the electrode isolated from the cathode in the cathode container receives the total applied amount of current (calculated in Coulomb), which is applied to the anode and the isolated electrode in the anode container. This method has been proven effective to remove even hard coatings on the cathode, and it may be used in combination with alternating polarity.

In a special embodiment of the apparatus according to the invention, a cathodic protected hot water container is used as a first container connected as cathode, i.e. a hot water container is used, which is connected as cathode and which is provided with at least one anode. Preferably, as a second container, such is used which on the inner walls is coated with, or mainly consist of, an electrical isolating material and which comprises at least one anode placed, relative to at least one electrode comprising alkaline sensitive metal and isolated from the anode, such that at least a part of the water flowing through the container passes between, the electrodes in the hot water container and the electrical isolated electrodes in the other container electrically being connected. The electrode in the hot water container can either be soluble, i.e. comprise alkaline sensitive metal, preferably aluminium, or insoluble. If the electrode is soluble, positive ions of alkaline sensitive metal are released, which locally, in

the hot water container, have a possible corrosion protecting effect. If the electrode is permanent the well-known cathodic protection is obtained.

The advantage of the above mentioned embodiment of the apparatus according to the invention is primarily, that the same electrical circuit may be used both to corrosion protection of a hot water container in a water system and for corrosion protection of the following water system by production of the negative ions of alkaline sensitive metal suited for this purpose. Further, a large number of existing water systems comprising a cathodic protected hot water container can be upgraded by either the mounting of another container of the above mentioned type on the hot water container, or by providing such further container in the following water system.

After some use of the apparatus described in the above mentioned embodiment, formation of deposits may appear in the other container comprising the at least one anode. With regard to avoiding or removing the deposits it is advantageous to alternate the polarity of the at least one anode in the container, such that the electrode operating as anode in one time period, changes polarity to cathode in another time period. Preferably the cathodic potential of the hot water container, and the potential of the at least one electrode in the hot water container is maintained constant during the changing polarity of the anode to avoid corrosion of the hot water container.

The present invention also relates to an apparatus part for corrosion protection of a water system, which apparatus part comprises a container, fully or partly flown through by the water, comprising at least one anode connected to a DC source, which apparatus part being characterized in that at least one electrode, comprising alkaline sensitive metal and electrically isolated from the anode connected to the DC source, is provided such that at least a part of the electrical current running in the water from the anode to an external cathode, is forced through the electrode comprising alkaline sensitive metal.

While the present invention so far has been described in connection with corrosion protection of a water system, the skilled person will understand the general use of the underlying process for production of ions of alkaline sensitive metal in an aqueous environment, by causing that at least a part of the current running from an anode to a cathode is forced through an electrode comprising alkaline sensitive metal isolated from cathode and anode.

The invention will be illustrated below by embodiments referring to the attached drawings, wherein

- Figure 1 discloses a vertical cross-sectional view of an apparatus according to the invention, wherein the container is used as cathode,
 Figure 2 discloses the apparatus of Fig. 1 in a horizontal cross-sectional view,

- Figure 3 discloses a horizontal cross-sectional view of a device for introduction into a container already existing in the water system,
- Figure 4 discloses a vertical cross-sectional view of the embodiment from Fig. 3,
- Figure 5 discloses a vertical cross-sectional view of a container of a material, which is not electrically conducting, wherein an electrically isolated electrode comprising alkaline sensitive metal is placed between an anode and a cathode in the container,
- Figure 6 discloses the apparatus from Fig. 5 in a horizontal cross-sectional view,
- Figure 7 discloses a refracted perspective drawing of an embodiment, where anode and cathode are separate by a partition wall in the same container,
- Figure 8 discloses a schematic cross-sectional view of an embodiment, where anode and cathode is provided in two separate containers,
- Figure 9 discloses a schematic cross-sectional view of an embodiment, where a container is provided in a water system with a cathodic protected hot water container,
- Figure 10 discloses a schematic cross-sectional view of an embodiment, where an anode container is provided on a hot water container with cathodic protection.

In the apparatus disclosed in Fig. 1 the water is introduced into a container 1 through an opening 2. The container comprises a permanent anode 3 and two electrodes 4 comprising alkaline sensitive metal, especially aluminium. The electrodes 4 are electrically isolated from the container with an insulating material 6. The water is discharged through an outlet 5. The container 1 is electrically connected as cathode, and the anode 3 is connected as anode. On the drawing the current direction is illustrated by arrows, which passes from the anode through the alkaline sensitive metal to the cathode.

On Fig. 2 the apparatus from Fig. 1 is disclosed from above. To avoid the current to run round the alkaline sensitive metal 4, two of the walls in the container is provided with an electrically isolating material 7.

Fig. 3 discloses an embodiment according to the invention, where a device is inserted in an existing container. The device is of two pieces of flat bar 9, which is welded on the inner wall of the container 1, wherein aluminium material, anode and aluminium material are placed in the successive order between the two pieces of flat bar 9. The two pieces of aluminium material are electrically isolated from both cathode and anode of an electrically isolating plate 8, onto which they are installed.

Fig. 4 discloses a possible placing of the devices shown in Fig. 3 in a hot water container.

Fig. 5 discloses an apparatus, where the water is introduced into a container 1 through the opening 2. The container consists of a insulating material. The container comprises an aluminium electrode 4 placed between a permanent anode 3 and a permanent cathode 10. The electrode 4 is electrically isolated from the container with an insulating material 6. The anode 3 and the cathode 10 is connected to a DC source.

On Fig. 6 the apparatus from Fig. 5 is disclosed in a horizontal cross-sectional view.

Fig. 7 discloses an apparatus, where a container 1 is separated by a partition wall 11 in a cathode chamber 12 and an anode chamber 13. The cathode chamber 12 is provided with a spiral-shaped cathode 10 connected to a negative pole on a not shown DC source. The cathode 10 is placed around an aluminium electrode 4 without coming into contact with it and the aluminium electrode is isolated from the container by an insulating material 6. The anode chamber is constructed in the same way as the cathode chamber, an anode 3 being provided instead of a cathode. The two aluminium electrodes 4 in the anode chamber and in the cathode chamber are electrically connected.

While operating, the polarity may, if desired, be alternated constantly or according to requirement, so the electrodes functioning as anode and cathode, respectively, in one time period change polarity to cathode and anode, respectively, in another time period. Furthermore, it might be desirable constantly or according to requirement, possibly in combination with operating with alternating polarity, to apply a positive voltage to the aluminium electrodes 4 to prevent or eliminate coatings.

On Fig. 7 the partition wall is provided such that the two chambers are in liquid communication. However, this is no condition, as ions of aluminium independently are produced in the individual chambers, which means that the individual chambers may be connected with separate water systems or the same water system in different areas.

Fig. 8 discloses an apparatus separated in two containers, a cathode container 14 and an anode container 15. The cathode container 14 is provided with a spiral-shaped cathode 10 connected with a negative pole on a not shown DC source. The cathode 10 is placed around an aluminium electrode 4 without coming into contact with it, and the aluminium electrode is isolated from the cathode container 14 by a insulating material 6. The anode container 15 is constructed in the same way as the cathode container, an anode 3 being provided instead of a cathode. The two aluminium electrodes in the anode container and cathode container are electrically connected.

While operating, the polarity may, if desired be alternated constantly or according to requirement, so the electrodes functioning as anode and cathode, respectively, in one time period may change polarity to cathode and anode, respectively, in another time period. Furthermore, it might be desirable constantly or according to requirement, possibly in combination with operating with

alternating polarity, to apply a positive voltage to the aluminium electrodes 4 to prevent or eliminate coatings.

On Fig. 8 the two containers are shown as being in liquid communication. However, this is no condition, as ions of aluminium independently are produced in the individual containers, which means that the individual containers may be connected with separate water systems or the same water system in different areas.

On Fig. 9 a hot water container 17 is used as cathode, as the hot water container 17 is connected with the negative pole on a DC source. In the same water system an anode container 15, comprising a spiral-shaped anode 3 connected with the positive pole on a DC source, is provided, the anode being placed around an aluminium electrode 4 isolated from the anode container 15 by a insulating material 6. The aluminium electrode 4 is electrically connected with another aluminium electrode 16 placed in the hot water container 17. The anode container is supplied with a constant flow rate by the pump 18.

In the anode container aluminate ions, for protection of the water system, are produced and in the hot water container positive aluminium ions are produced, which are presumed to be inhibitors to local corrosion of the hot water container. If the presence of a soluble aluminium electrode in the container causes a too big siltation, a insoluble electrode may alternatively be used.

While operating, the polarity of the anode may, if desired, be change, if a formation of coating occur. Such change of the polarity may for example be periodic or may be carried out according to requirement. If an alternation of the polarity of the anode is carried out, the anode container on the inside has to be coated with, or mainly consists of, an electrically inert material, i.e. an electrically isolating material to avoid corrosion of the container.

Regardless the change of polarity in the anode container, it has to be ensured that the potential of the hot water container remains cathodic, otherwise corrosion of the hot water container will occur. Also, it must be ensured that the electrode 16 maintain its capability as an anode so that the hot water container continues to be cathodically protected. This may be obtained by a proper design of the electronics in the control unit, which usually constitutes the DC source.

Fig. 10 discloses an embodiment, where an anode container 15 has been mounted on an existing cathodically protected hot water container 17 in a water system. An aluminium electrode 4 in the anode container is electrically connected with a permanent electrode 19, which hereby obtains the capability as an anode. By this design of the apparatus according to the invention, the water system is supplied with aluminate ions from the anode container, at the same time as the hot water container continuously is protected against corrosion.

As for the embodiment on Fig. 9 the polarity of the anode may, if desired, be alternated. However, it has to be ensured that the hot water container at the same time remains cathodically protected.

Claims

1. An apparatus for corrosion protection of a water system comprising a container (1, 14, 17), fully or partly flown through by water, connected as cathode and/or comprising at least one cathode (9, 10), the apparatus being provided with at least one anode (3), wherein cathode and anode are connected to a DC source, characterized in that at least one electrode (4), comprising alkaline sensitive metal and electrically isolated from the cathode and the anode connected to the DC source, is provided such, that at least a part of the electrical current, running in the water from the anode to the cathode, is forced through the electrode comprising alkaline sensitive metal.
2. An apparatus according to claim 1, characterized in that the alkaline sensitive metal is selected among aluminium, zinc, tin or lead, or mixtures thereof, preferably aluminium.
3. An apparatus according to claim 1 or 2, characterized in that the anode is placed in the same container as the cathode and/or in the container connected as cathode, and that electrically isolated alkaline sensitive metal is placed between cathode and anode.
4. An apparatus according to claim 1 or 2, characterized in that the at least one anode is placed in the same container as the at least one cathode and in that the container is divided into two chambers, wherein the first chamber (12) comprises at least one cathode (10) and at least one electrode (4) electrically isolated from the cathode, and the second chamber (13) comprises at least one anode (3) and at least one electrode (4) electrically isolated from the anode and comprising alkaline sensitive metal, the electrodes, isolated from cathode and anode in the two chambers, being electrically connected.
5. An apparatus according to claim 1 or 2, characterized in that it comprises two containers, wherein the first container (14, 17) is connected as cathode, and/or comprises at least one cathode, and comprises at least one electrode (4, 16, 19) electrically isolated from the cathode, and the second container (15) comprises at least one anode and at least one electrode electrically isolated from the anode and comprising alkaline sensitive metal, the electrodes, isolated from cathode and anode in the two containers, being electrically connected.
6. An apparatus according to claim 5, characterized in that the inner wall of both containers are coated with, or the containers mainly consist of, electrically isolating material, wherein at least one cathode in the first container is placed such relative to at least one electrode comprising alkaline sensitive metal, that

at least a part of the water flowing through the container passes between, and wherein at least one anode in the second container is placed such relative to at least another electrode comprising alkaline sensitive metal, that at least a part of the water flowing through the container passes between, the electrodes isolated from anode and cathode and comprising alkaline sensitive metal being electrically connected.

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7. An apparatus according to claim 1-6, characterized in that it is operated with alternating polarity, such that the electrodes operating as anode and cathode, respectively, in one time period changes polarity to cathode and anode, respectively, in another time period.

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8. An apparatus according to claim 7, characterized in that it is operated with alternating current.

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9. An apparatus according to claim 5, characterized in that the first container (17) is connected as cathode and comprises at least one electrically isolated electrode (16,19) either comprising alkaline sensitive metal or being insoluble, and that the second container (15) on the inner wall is coated with, or mainly consist of, an electrically isolating material, said second container comprising at least one anode (3) placed such, relative to the at least one isolated electrode (4) comprising alkaline sensitive metal, that at least a part of the water flowing through the container passes between, the electrodes, electrically isolated from cathode and anode in the two containers, being electrically connected.

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10. An apparatus according to claim 9, characterized in that the polarity of the at least one anode in the second container may alternate, such that the electrode in this container operating as anode in one time period changes polarity to cathode in another time period.

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11. An apparatus according to claim 1-10, characterized in that the at least one electrode comprising alkaline sensitive metal is applied with a positive potential.

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12. An apparatus part for corrosion protection of a water system comprising a container (15), fully or partly flown through by the water, comprising at least one anode (3) connected to a DC source, characterized in that at least one electrode (4), comprising alkaline sensitive metal and electrically isolated from the anode connected to the DC source, is provided such, that at least a part of the electrical current, running in the water from the anode to an external cathode, is forced through the electrode comprising alkaline sensitive metal.

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13. A process for production of ions of alkaline sensitive metal in an aqueous environment, characterized in that at least a part of the current, running from an anode to a cathode, is forced through an electrode comprising alkaline sensitive metal isolated from cathode and anode.

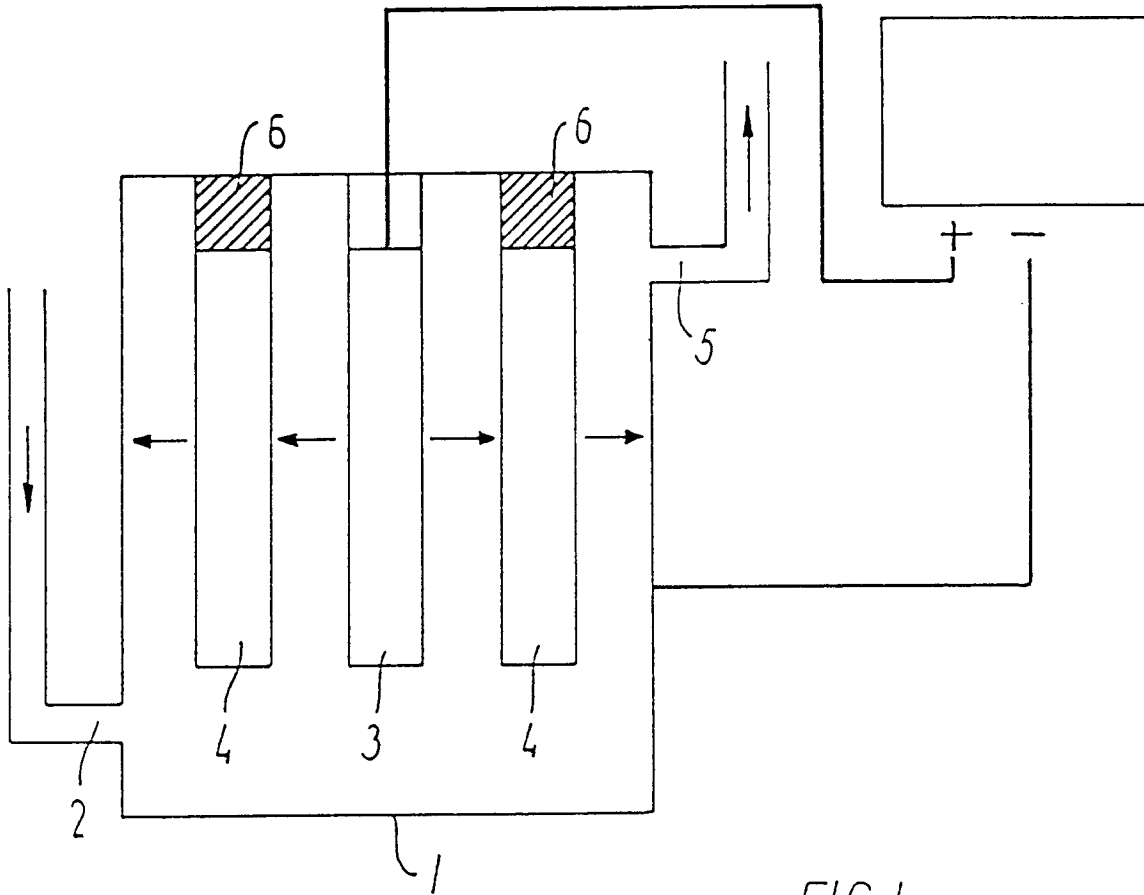


FIG. 1

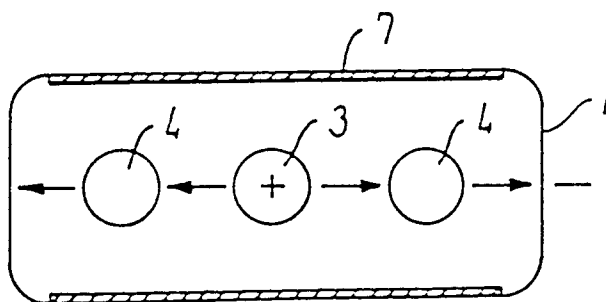
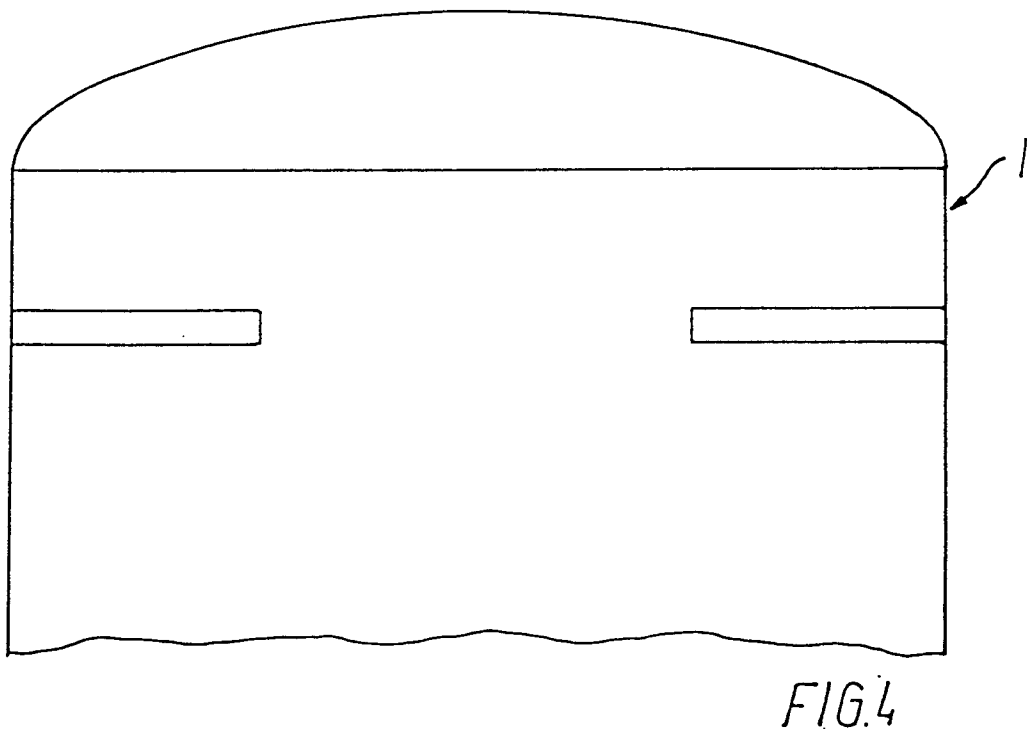
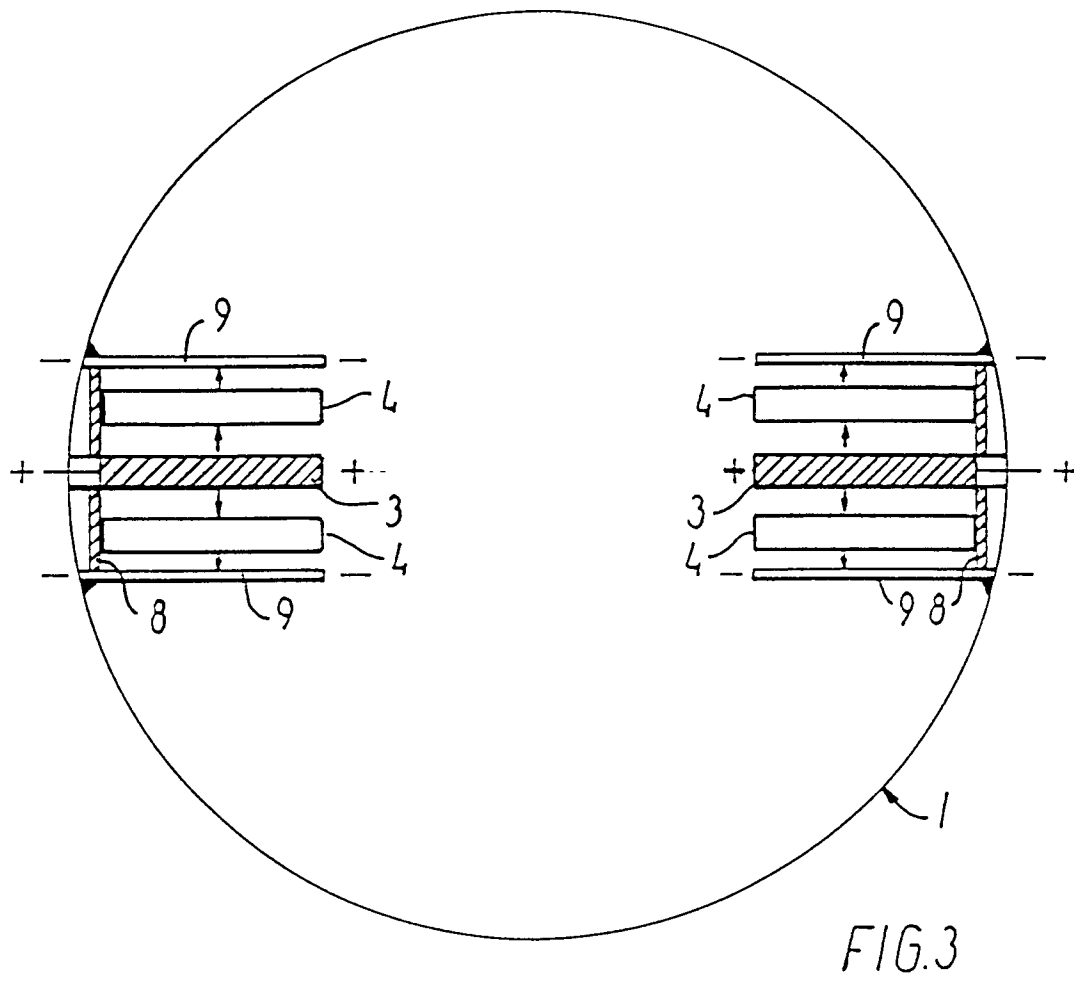


FIG. 2



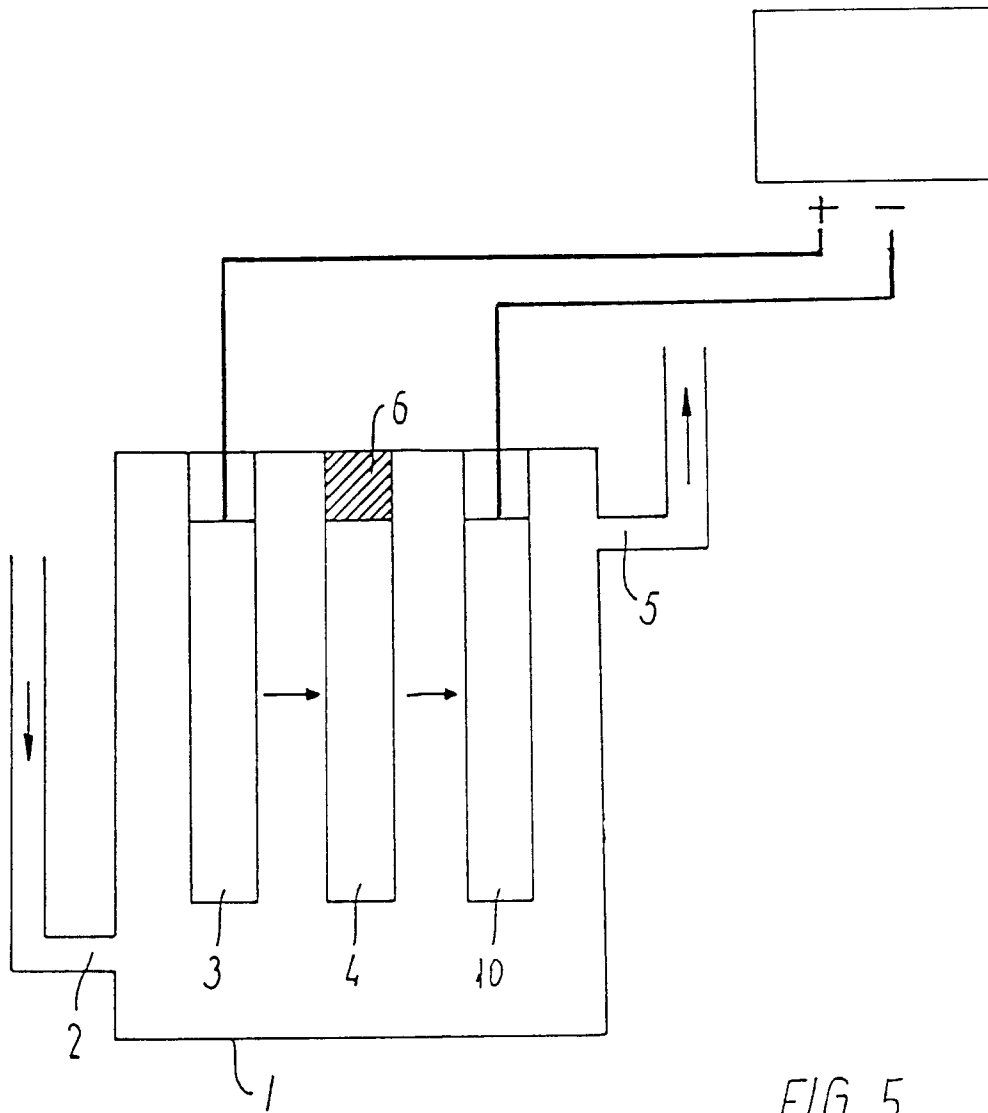


FIG. 5

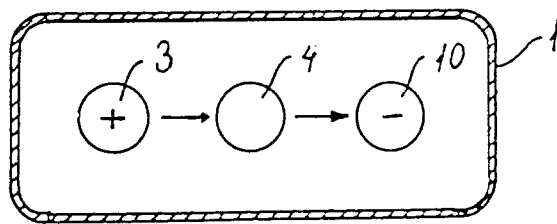


FIG. 6

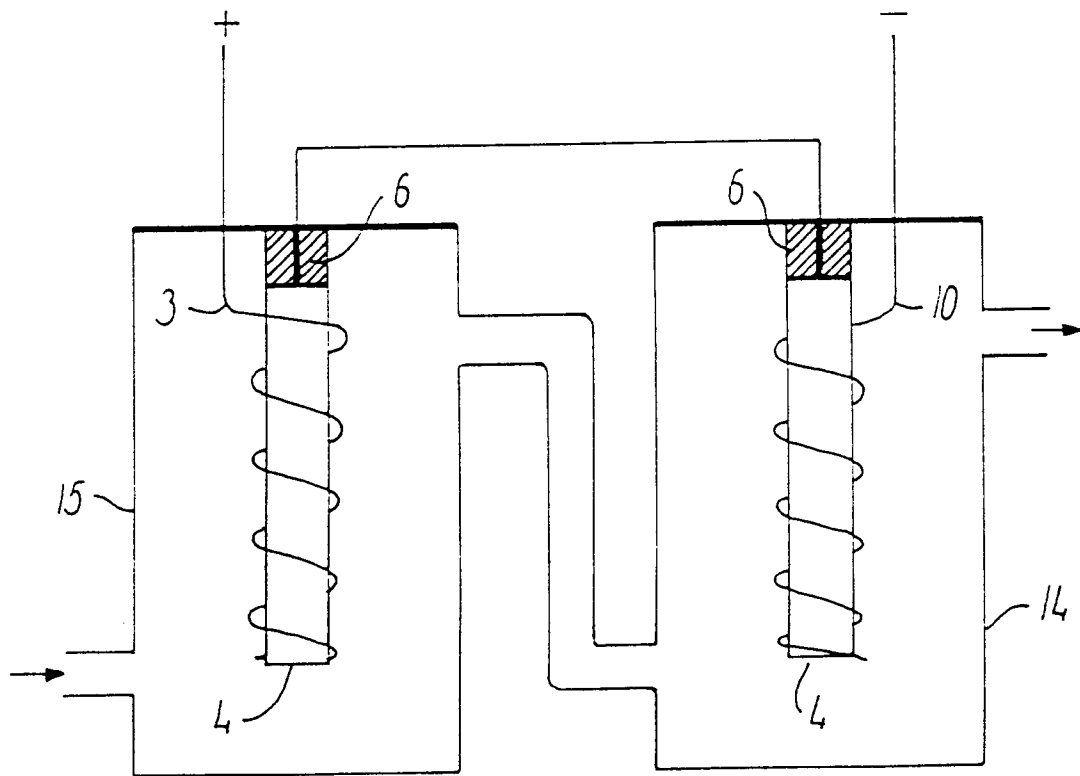
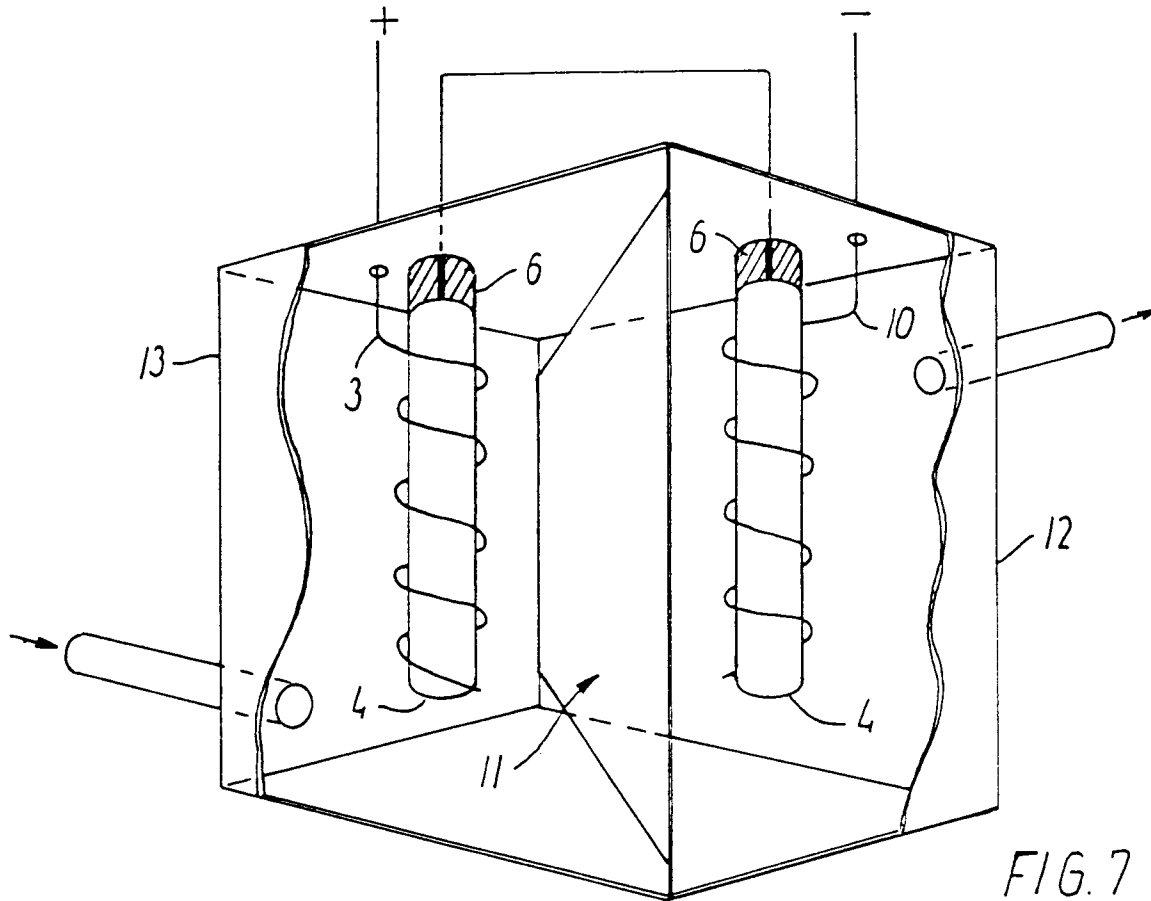


FIG. 8

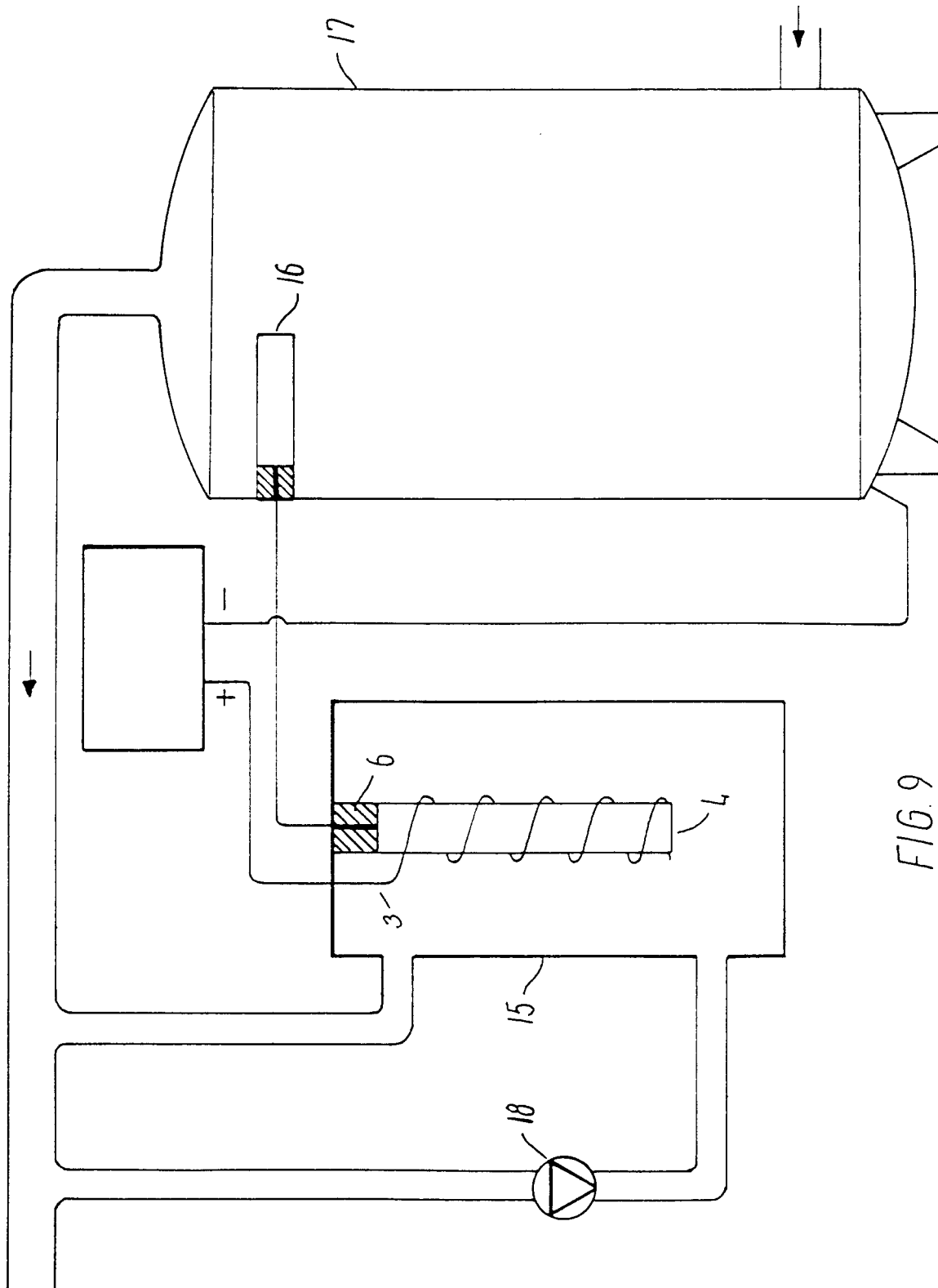


FIG. 9

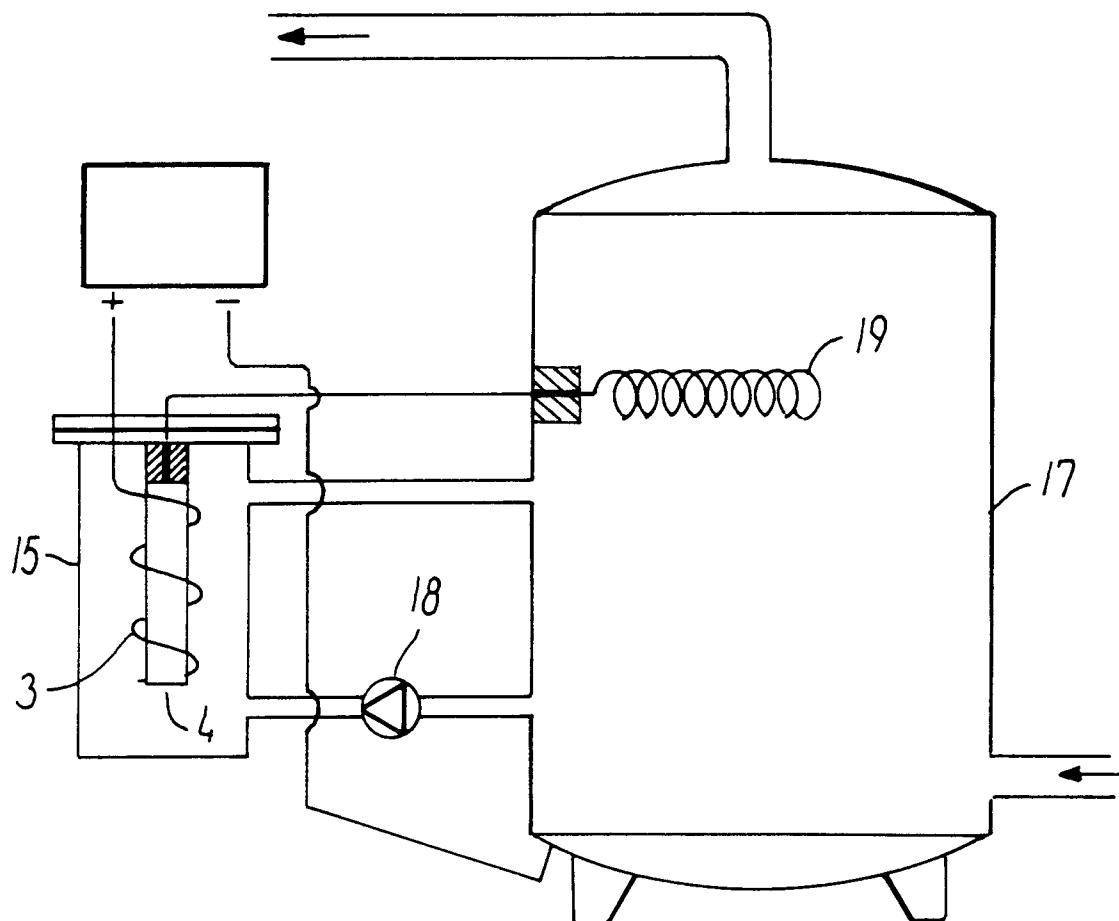


FIG. 10



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 61 0001

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.6)
Y	WO-A-91 14018 (I. KRÜGER AS) 19 September 1991 * page 4, line 28 - page 6, line 16 * * page 9; claims 1-6 * * figures 1-3 *	1,2,7,11	C23F13/02
Y	FR-A-1 418 867 (S. SEURAT) * page 4 - page 5; claims 1-5 *	1,2,7,11	
A	DE-A-24 45 903 (GULDLAGER ELECTROLYSE GMBH & CO KG) 13 November 1975 * column 1 - column 2; claims 1-18 * * column 7, line 4 - line 14 * * figure 1 *	1	
D,A	US-A-5 344 537 (C. FABRICIUS) 6 September 1994 * column 3 - column 4; claims 1,2 *	1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C23F
Place of search		Date of completion of the search	Examiner
THE HAGUE		12 April 1996	Groseiller, P
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