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(72) Inventors:  
• **Kholky, Mounir**  
**48006 BILBAO (ES)**  
• **Nazabal Muñagorri, Luis Ma**  
**20493 ELDUAIN (ES)**

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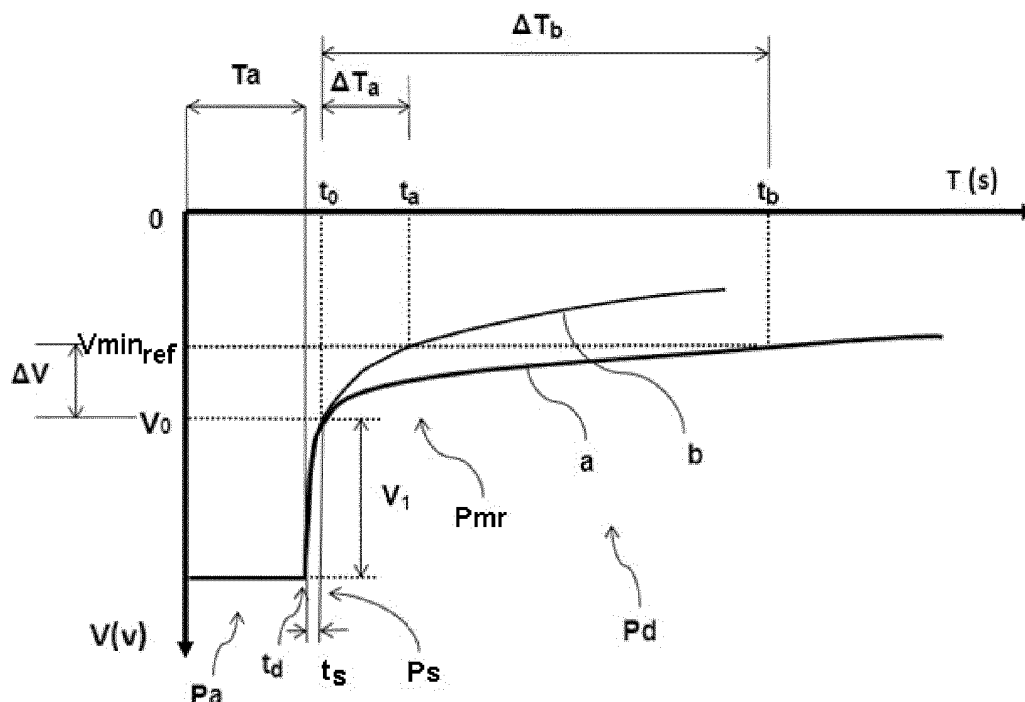
(74) Representative: **Igartua, Ismael**  
**Galbaian S.Coop.**  
**Polo de Innovación Garaia**  
**Goiru Kalea 1 - P.O. Box 213**  
**20500 Arrasate-Mondragón (ES)**

(71) Applicant: **Fagor, S. Coop.**  
**20500 Arrasate-Mondragon (ES)**

(54) **Method and device for anti-corrosion cathodic protection**

(57) The present invention relates to a method and device for impressed current anticorrosion cathodic protection for metal surfaces in contact with an electrolyte, in which the following is used: an inert anode, wherein a protection current is connected and disconnected in successive periods  $P_a$  and  $P_d$ , each period  $P_d$  comprising a standby phase  $P_s$ , and a measurement and regulation phase  $P_{mr}$  in which a potential difference  $\Delta V$  between

the potential  $V_0$  in the inert anode and the metal surface is measured, and a potential  $V_{minref}$  is measured, wherein in phase  $P_{mr}$  the time  $\Delta T$  elapsing between an instant  $t_0$  in which the potential  $V_0$  is measured and an instant  $t$  in which the  $V_{minref}$  is reached is measured, and the magnitude of the protection current and an activation time  $T_a$  of the next period  $P_a$  is established depending on  $\Delta V$  and  $\Delta T$ .



**Fig. 1**

## Description

### TECHNICAL FIELD

**[0001]** The present invention relates to methods for impressed current anti-corrosion cathodic protection for use on metal surfaces in contact with an electrolyte, particularly hot water accumulator tanks, and devices suitable for implementing said methods to maintain protection.

### PRIOR ART

**[0002]** Methods referring to impressed current cathodic or electronic anode protection preventing electrochemical corrosion are known in the state of the art; this protection is related to metal surfaces which are in contact with an electrolyte or medium which is capable of conducting electricity, and particularly with hot water accumulator tanks.

**[0003]** Said methods are aided by an external protection current which is impressed on the metal surface to be protected and use an inert anode acting as a reference electrode when the potential of said anode is measured with respect to the potential of the surface to be protected, and as an anode of the impressed protection current transmitting said current through the electrolyte to said surface; said methods also use a control and regulation unit performing measurement, processing and subsequent regulation functions. The protection current is periodically disconnected and the potential existing between the inert anode and the metal surface is measured, being compared with the reference protection potential of the metal surface.

**[0004]** Patent ES2020584 B3 describes a method and device for anti-corrosion cathodic protection for metal surfaces in contact with an electrolyte, with the aforementioned features. The protection current is periodically disconnected, there being in each disconnection period a standby phase in which, and after a very short time interval, the potential existing between the inert anode and the metal surface to be protected is measured; there is a regulation phase after the standby phase in which the measured potential is compared with the reference protection potential of the metal surface, and the difference is used as magnitude regulated in the regulation phase for the protection current in the next activation period.

### DISCLOSURE OF THE INVENTION

**[0005]** The object of the invention is to provide a method for impressed current anti-corrosion cathodic protection for use on metal surfaces in contact with an electrolyte and a device suitable for implementing said method to maintain protection, as described in the claims. This invention can be applied both in hot water accumulator tanks and in any other context in which there are metal

surfaces subjected to conditions that may cause corrosion.

**[0006]** One aspect of the invention therefore relates to a method for impressed current anti-corrosion cathodic protection with the aid of an external protection current, said method using an inert anode acting as a reference electrode and as an anode of the protection current, wherein the protection current is connected in activation periods and disconnected in disconnection periods, each disconnection period comprising a standby phase and a measurement and regulation phase after the standby phase in which a potential difference  $\Delta V$  between a potential existing between the inert anode acting as a reference electrode and the metal surface is measured, and a minimum reference protection potential of the metal surface is measured; in the measurement and regulation phase the time  $\Delta T$  elapsing between an instant in which the potential is measured and an instant in which the minimum reference protection potential of the metal surface is reached is measured, and the magnitude of the protection current and an activation time of the next activation period is established depending on the potential difference  $\Delta V$  and time  $\Delta T$ .

**[0007]** Another aspect of the invention relates to a device suitable for implementing a method for impressed current anti-corrosion cathodic protection with the aid of an external protection current, comprising the inert anode acting as a reference electrode and as an anode of the protection current, and a control and regulation unit measuring the potential difference  $\Delta V$  produced between the potential existing between the inert anode acting as a reference electrode and the metal surface when the protection current is interrupted, and a minimum reference protection potential of the metal surface set in the control and regulation unit; said device progressively adapts to the causes producing corrosion, the control and regulation unit measuring the time  $\Delta T$  elapsing between the instant in which the potential is measured and the instant in which the minimum reference protection potential of the metal surface is reached, and establishing the magnitude of the protection current and the activation time of the next activation period depending on the potential difference  $\Delta V$  and time  $\Delta T$ .

**[0008]** A method and a device implementing said method which allow maintaining anti-corrosion cathodic protection of a metal surface in contact with an electrolyte, as is the case of a hot water accumulator, automatically regulating the protection potential of said surface, maintaining it in an ideal protection zone, without any prior manual adjustment of the minimum reference protection potential of the metal surface, are obtained. Since the time  $\Delta T$  elapsing until reaching the minimum reference protection potential of the metal surface is also measured in the process of measuring the potential to which the surface to be protected is subjected, the ratio of the potential difference  $\Delta V$  and time  $\Delta T$  values allows periodically knowing their evolution; this information reflects the evolution of the external causes of corrosion affecting

the surface to be protected and which can sustain unexpected changes due to a number of uncontrollable factors. Depending on the  $\Delta V$  and  $\Delta T$  values measured in each disconnection period of the protection current, the control and regulation unit defines the suitable protection current for the next activation period to maintain the surface in an ideal protection zone and the activation time of said current, such that it prevents both low protection and over-protection of said surface over time, automatically regulating said values.

**[0009]** These and other advantages and features of the invention will become evident in view of the drawings and the detailed description of the invention.

## DESCRIPTION OF THE DRAWINGS

### [0010]

Figure 1 shows a graph depicting the evolution of potential  $V$  in volts (v) with respect to time  $T$  in seconds (s) of a metal surface in two situations with different causes of corrosion, both starting from the same protection potential  $V$  value and with the same activation time  $T_a$ , and the protection current  $I$  being interrupted.

Figure 2 shows a flowchart of an embodiment of the method for impressed current anti-corrosion cathodic protection of the invention.

Figure 3 shows a graph depicting an operating example of the embodiment of the method for impressed current anti-corrosion cathodic protection of the invention depicted in Figure 2, showing in a related manner different activation periods  $P_a$  and disconnection periods  $P_d$  with the evolution of the potential  $V$  in volts (v) with respect to time  $T$  in seconds (s) in a top graph, and the evolution of the protection current  $I$  in milliamperes (mA) over time  $T$  in seconds (s) in a bottom graph.

Figure 4 shows a schematic view of the main parts of an embodiment of a device for impressed current anti-corrosion cathodic protection of the invention.

## DETAILED DISCLOSURE OF THE INVENTION

**[0011]** The electrochemical corrosion process, in which a metal material loses some of the energy acquired during transformation processes and returns to its original state as found in nature and rusts, has been known for some time. Electrochemical corrosion is therefore the deterioration of a metal material in which simultaneous electricity transport from certain areas of a metal surface to other areas through a medium capable of conducting electricity takes place. In said process the metal that becomes rusty loses electrons which are conducted through the medium to other stronger materials, i.e., with

a higher potential.

**[0012]** Provided that there are two materials in contact through a medium capable of conducting electric current, the material with the lower potential will lose electrons, and the material with a higher potential will gain them. There are different methods to prevent corrosion, including taking measurements on the conductive medium by removing  $O_2$  from water or chlorine ions, performing actions on parts acting on design and materials, electrode coating such as with the protective enamel in hot water accumulator tanks, and electrochemical protection by using sacrificial anodes or impressed current anodes.

**[0013]** The present invention relates to a method for impressed current anti-corrosion cathodic protection suitable for use on metal surfaces in contact with a medium or electrolyte, particularly in hot water accumulator tanks, and the device suitable for implementing said method to perform the protection. In this method for protecting against corrosion, the surface to be protected is connected to the negative pole of an external direct current generator, and the positive pole of said source is connected to a current dispersive electrode. This current supplied by the external direct current source is used to impress the necessary current on the surface to be protected, the circuit being closed through the electrolyte, electrochemical reactions taking place between the metal surface and the electrolyte and between the electrolyte and the current dispersive electrode allowing electron circulation; this electron excess on the metal surface allows said surface to have a specific potential and gets said surface to perform as a cathode.

**[0014]** The object of this method for impressed current cathodic protection is for the metal surface to be protected to constantly work as a cathode, with a potential in the order of  $-0.8$  v in the case of treated industrial use iron with respect to the reference silver/silver chloride ( $Ag/AgCl$ ) electrode, a value with which it is in a situation of equilibrium, and outside of this value, if it is lower it can be over-protected against corrosion and bring about problems such as premature dispersive electrode wear or an  $H_2$  excess, and if it is higher it can enter a corrosion zone.

**[0015]** The method for impressed current anti-corrosion cathodic protection of the invention for metal surfaces 2 in contact with an electrolyte 3 has the aid of a protection current " $I$ " supplied by an external direct current generator. Said method uses an inert anode 4 acting as a reference electrode and as a protection current " $I$ " dispersive anode. As can be seen in Figure 3, the method comprises different activation periods " $P_a$ " in which the protection current " $I$ " is supplied during an activation time " $T_a$ ", and the metal surface 2 is subjected to a protection potential " $V$ "; after each activation period " $P_a$ " the method comprises a disconnection period " $P_d$ ", in which the protection current " $I$ " is interrupted. As can be seen in Figure 1, each of the disconnection periods " $P_d$ " in turn comprises a standby phase " $P_s$ " during a time " $t_s$ " in which a voltage drop " $V_1$ " due to Ohm's law takes place from

the protection potential "V" until reaching a potential "Vo" existing between the inert anode 4 acting as a reference electrode and the metal surface 2 to be protected; the disconnection period "Pd" also comprises a measurement and regulation phase "Pmr" after the standby phase "Ps" in which the potential difference  $\Delta V$  ( $\Delta V = V_o - V_{\text{minref}}$ ) produced between the potential "Vo" and the minimum reference protection potential "Vminref" of the metal surface 2 previously defined is measured. In said measurement and regulation phase "Pmr" the time  $\Delta T$  elapsing between an instant "to" in which the potential "Vo" is measured and an instant "t" in which the potential "Vminref" is reached is further measured, establishing the magnitude of the protection current "I" and an activation time "Ta" for the next activation period "Pa" depending on the potential difference  $\Delta V$  and time  $\Delta T$ . The disconnection period "Pd" is observed in greater detail in Figure 1 where the time scale is not respected because the standby time "ts" is insignificant compared with time  $\Delta T$ , so the standby phase "Ps" could not be seen on the time scale of Figure 3.

**[0016]** Figure 1 shows a graph depicting the evolution of the potential "V" in volts (v) over time "T" in seconds (s) of a metal surface 2 in two different situations; both situations are different in that the metal surface 2 is subjected to different external causes of corrosion, these situations being reflected in two curves starting from the same protection potential "V" value, and with the same activation time "Ta" of the protection current "I"; the protection current "I" is then interrupted in a disconnection instant "td", and the standby time "ts" is left to elapse, allowing the potential drop "V1" due to Ohm's law to occur. When the standby time "ts" has elapsed instant "to" is reached where the residual potential between the inert anode 4 and the metal surface 2 is "Vo", which is the voltage polarized in the inert anode 4; the time  $\Delta T$  elapsing until an instant "t" in which in both situations the minimum reference potential "Vminref" of the metal surface 2 to be protected is reached starts to be measured in said instant "to". The obtained curves are "a" and "b" and they have different times  $\Delta T_a$  and  $\Delta T_b$  because the external corrosion conditions to which they have been subjected are different; this means, for example, that curve "a" represents a slower evolution of the potential difference  $\Delta V$  over time  $\Delta T_a$  than the evolution of the potential difference  $\Delta V$  over time  $\Delta T_b$  of curve "b"; this is because the times taken to reach "Vminref" are different, meaning that the metal surface 2 in situation "a" is well-protected because electrons take longer to disappear, and in situation "b" it is not as well protected, reflecting that the external causes of corrosion are stealing many electrons and the potential drops faster. This evolution of the potential drop over time is also known as "corrosion rate".

**[0017]** Figure 2 shows a flowchart of an embodiment of the method for impressed current anti-corrosion cathodic protection of the invention, and Figure 3 shows a graph depicting an operating example of the embodiment of the method depicted in Figure 2, showing in a related

manner different activation periods "Pa" and disconnection periods "Pd" with the evolution of the potential "V" in volts (v) over time "T" in seconds (s) in a top graph, and the evolution of the protection current "I" in milliamperes (mA) over time "T" in seconds (s) in a bottom graph.

**[0018]** The depicted method starts when a disconnection period "Pd" starts after any one activation period "Pa", with a specific protection current "I" and a specific activation time "Ta", has elapsed; the standby phase "Ps" starts in disconnection instant "td", in which instant the protection current "I" is interrupted and a time "ts" is left to elapse. A potential drop "V1" due to Ohm's law from the protection potential "V" until reaching the potential "Vo" existing between the inert anode 4 acting as a reference electrode and the metal surface 2 to be protected, occurs in that time.

**[0019]** A measurement and regulation phase "Pmr" in which the potential difference  $\Delta V$  produced between the potential "Vo" and the minimum reference protection potential "Vminref" of the metal surface 2 previously defined is measured then starts within the disconnection period "Pd". In said measurement and regulation phase "Pmr" the time  $\Delta T$  elapsing between the instant "to" in which the potential "Vo" is measured and an instant "t" in which the potential "Vminref" is reached is further measured.

**[0020]** In an exemplary embodiment of the device implementing the method of the invention applied on the metal surface of a hot water accumulator tank, the inert anode 4 can be an electrode made with titanium and covered with noble metals. The reference protection potential "Vminref" in the case of treated industrial use iron, and at a temperature of 25°C, is in the order of -0.8 v, value with which it is in situation of equilibrium, and measured in reference to a silver/silver chloride (Ag/AgCl) reference electrode. Since the electrode is a titanium electrode covered with noble metals in this example, the reference goes from the reference electrode to the titanium electrode, resulting in a potential "Vminref" value of iron in the order of -1.9 v. Continuing with the mentioned example, and setting the water contained in the hot water accumulator tank at 40°C, the potential drop "V1" is in the order of -0.2 v until reaching a potential "Vo" of -1.9 v. In the exemplary embodiment considered for the hot water accumulator tank, the protection current "I" can be between approximately 0 mA and approximately 6 mA, and the activation time "Ta" can be between approximately 5 s and approximately 60 s, depending on the volume of the tank, the conditions of the surrounding environment and acquired experience.

**[0021]** If the potential difference  $\Delta V$  is positive and therefore the potential "Vo" is greater than the reference potential "Vminref", it means that the metal surface 2 to be protected is in a corrosion zone and some external cause is provoking that electron theft. An increment of the protection current "I" is established in such case to supply electrons to the surface 2 and convert it into a cathode, and this is done during a predefined minimum activation time "Ta" for the next activation period "Pa",

being able to obtain such values empirically and they range depending on the conditions of the surrounding environment. Then, and after the activation period "Pa" has elapsed, a measurement of  $\Delta V$  and of  $\Delta T$  is taken again in the next measurement and regulation phase "Pmr".

**[0022]** If the potential difference  $\Delta V$  is negative, and therefore the potential "Vo" is less than the reference potential "Vminref", it means that the metal surface 2 to be protected is in an immune zone, but it is necessary to check with the measured time  $\Delta T$  what protection zone the metal surface 2 is in to take measurements; i.e., if it is in an over-protected zone, if it is in an ideal protection zone, or if it is in a low protection zone. Protection in one of these zones can be located automatically with the time  $\Delta T$  measurement, and it is compared with time pre-established values. This evolution of potential over time, referred to as corrosion rate, is therefore the decision-making basis in the present method. The reference potential "Vminref" value of the metal surface 2 is defined as a level that is slightly under a corrosion limit "Lc" for said metal surface 2 and after this level and higher it enters the corrosion zone. Then, and in the next disconnection period "Pd", a new measurement of  $\Delta V$  and  $\Delta T$  is taken and the new protection current "I" and activation time "Ta" values are established for the next activation period "Pa", progressively aiming for times  $\Delta T$  that are close to a reference time "tr" that is empirically obtained, and thereby allows the metal surface 2 to be in the ideal protection zone.

**[0023]** If the potential difference  $\Delta V$  is negative and the measured time  $\Delta T$  has a value less than a predefined time "t1", it is understood that the metal surface 2 is not sufficiently protected and urgently needs a larger electron load supplied by the protection current "I" and thereby preventing said surface 2 from entering the corrosion zone; an increment of the protection current "I" during a minimum predefined activation time "Ta" is established in such case for the next activation period "Pa", a measurement of  $\Delta V$  and of  $\Delta T$  is taken again in the next measurement and regulation phase "Pmr".

**[0024]** If the potential difference  $\Delta V$  is negative and the time  $\Delta T$  has a value greater than a defined time "t2", also empirically obtainable, it is understood that the metal surface 2 is sufficiently, even excessively, protected, and urgently needs a lower electron load supplied by the protection current "I" so that it does not produce unwanted effects; a reduction of the protection current "I" during a predefined minimum activation time "Ta" is established in such case for the next activation period "Pa". Then, and after the activation period "Pa" has elapsed, a measurement of  $\Delta V$  and of  $\Delta T$  is taken again in the next measurement and regulation phase "Pmr".

**[0025]** If the potential difference  $\Delta V$  is negative and the time  $\Delta T$  has a value greater than the defined time "t1", and less than the defined time "t2", it is understood that the metal surface 2 is in the ideal protection zone and needs another reference to more specifically define the

protection level and progressively take said protection to the optimum level. The measured time  $\Delta T$  is compared with the reference time "tr", and if it is less a protection current "I" maintenance and a slight increase of the activation time "Ta" are established for the next activation period "Pa". Then, and after the activation period "Pa" has elapsed, a measurement of  $\Delta V$  and of  $\Delta T$  is taken again in the next measurement and regulation phase "Pmr".

**[0026]** If the potential difference  $\Delta V$  is negative and the time  $\Delta T$  has a value greater than the defined time "t1", and less than the defined time "t2", it is understood that the metal surface 2 is in the ideal protection zone, and the measured time  $\Delta T$  is compared with the reference time "tr", and if it is greater a slight reduction of the protection current "I" and activation time "Ta" maintenance are established for the next activation period "Pa". Then, and after the activation period "Pa" has elapsed, a measurement of  $\Delta V$  and of  $\Delta T$  is taken again in the next measurement and regulation phase "Pmr".

**[0027]** The effect of temperature on the corrosion rate of a metal structure is known, and for that purpose the method for protection of the invention uses the measured temperature of the electrolyte 3. The minimum reference protection potential "Vminref" value of the metal surface 2 defined previously is corrected with said temperature in the measurement and regulation phase "Pmr". This allows establishing the protection current "I" and the activation time "Ta" for the next activation period "Pa". It has been defined that the reference protection potential "Vminref" in the case of treated industrial use iron, and at a temperature of 25°C, is in the order of -0.8 v in reference to a silver/silver chloride (Ag/AgCl) reference electrode, and it is -1.9 v when the titanium electrode is used as a reference at a water temperature of 40°C; in the mentioned example the measured water temperature is a mean temperature established between the values taken by one or more temperature sensors preferably situated in contact with the electrolyte. Taking into account mean temperature values during the hot water accumulator tank operation, and as a mere example as a guideline, the temperature can range between approximately a value less than 30°C, a value between approximately 30°C and approximately 50°C, a value between approximately 50°C and approximately 70°C, and a value greater than 70°C; minimum reference protection potential "Vminref" values of the metal surface 2 can range between approximately -1.95, -1.9, -1.85 and -1.8 v respectively. The protection current "I" adapted to the effect caused by temperature is established with the corrections made, which allows establishing a potential V suited to the metal surface 2 to be protected.

**[0028]** Another aspect of the invention relates to a device 1 suitable for implementing the method of the invention. The device 1 comprises the inert anode 4 acting as a reference electrode and as an anode of the protection current "I". When the potential of a material is measured an electrode made of a noble material, such as titanium

for example, is used and this same reference electrode is used as an impressed protection current dispersive anode; therefore, when the direct current generator is connected, said electrode transmits the protection current "I" sending the electron flow to the metal surface 2. Therefore, two functions are being performed with one and the same electrode, and two types of signals circulate through it, sending the protection current "I" to the electrolyte 3 from the direct current generator, and sending the signal of the potential "V" measured with the reference electrode to the device 1. A bushing 14 supporting the inert anode 4 and attaching the latter to the metal surface 2 to be protected, said bushing 14 being made of an insulating material, preferably plastic, is used to take the potential measurements with the inert anode 4 when the anode 4 acts as a reference electrode, and said potential measurement is not distorted by undue contacts with the metal surface 2 where the inert anode 4 is attached and does not provoke an electron theft and therefore a loss of protection potential.

**[0029]** The device 1 comprises a control and regulation unit 5, said control and regulation unit 5 measuring the potential difference  $\Delta V$  produced between potential "Vo" and potential "Vminref". The potential Vo existing between the inert anode 4 and the metal surface 2 to be protected when the protection current "I" is interrupted is reached after a very short standby time "ts", between approximately 30 microseconds and approximately 50 microseconds; said time is enough for the potential drop "V1" due to Ohm's law, " $V1 = I \times R$ ", where "R" is resistance of the electrolyte 3, to occur. The minimum reference protection potential "Vminref" of the metal surface 2 is different for each material used on the surface to be protected, and is defined with the aid of the electrochemical table of materials and experience, this reference potential "Vminref" being located in the immune area with respect to corrosion defined for said material in the Pourbaix diagram (not shown in the drawings); this predefined potential is set in the control and regulation unit 5 as a reference. The device 1 of the invention adapts progressively and immediately to the causes producing corrosion, external causes which are often completely unforeseeable, such as metal joints that are not completely insulated, leaking in of water with different pH characteristics, water temperature, etc., agents acting as electron thieves, a sufficient amount of which ultimately do not go to the metal surface 2 to be protected. To adapt to said conditions and maintain the metal surface 2 in the ideal protection zone, the device 1 measures the time  $\Delta T$  elapsing between the instant "to" in which the potential "Vo" is measured, and the instant "t" in which the minimum reference protection potential "Vminref" of the metal surface 2 is reached by means of the control and regulation unit 5, the control and regulation unit 5 establishing the magnitude of the protection current "I" and the activation time "Ta" of the next activation period, depending on the potential difference  $\Delta V$  and time  $\Delta T$ .

**[0030]** To perform these measurement and regulation

functions, the control and regulation unit 5 comprises, as can be seen in Figure 4, a control and processing unit "CPU" receiving input signals 6 from a potential measurement interface "PMI", processing them and emitting output signals 7 to a direct current generator "CCG"; the positive pole of the direct current generator "CCG" is connected to the inert anode 4, and the negative pole is connected to the metal surface 2 to be protected. The potential measurement interface "PMI" in turn continuously receives signals 8 corresponding to the potential of the inert anode 4 when it acts as a reference electrode and sends the input signals 6, after treating the signals 8, to the control and processing unit "CPU" so that it can identify them. The control and processing unit "CPU" processes the signals 6 received and further takes into account the time  $\Delta T$  measurements taken, and this together with the actuation parameters defined and set in the control and processing unit "CPU", allows processing the data set and defining the protection current "I" and activation time "Ta" for the next activation period; this definition of protection current "I" passes as signals 7 to the direct current generator "CCG" and generates the protection current "I", sending it to the inert anode 4, which allows establishing a suitable potential "V" between the anode 4 and the metal surface 2 to be protected. A diode 15 allowing the exit of the protection current "I" to the inert anode 4 but preventing signals 8 corresponding to the potential of the inert anode 4 from reaching the direct current generator "CCG" and being able to be diverted towards the potential measurement interface "PMI" is arranged at the output of the direct current generator "CCG". For assembly operation, the control and regulation unit 5 also comprises a power manager 9, comprising an electric energy interface "EEI" connected to the electrical grid 10, and in turn supplying energy to the control and processing unit "CPU"; this power manager 9 also comprises a rechargeable battery "BAT", supplied by the electric energy interface "EEI" and which can replace said interface "EEI" when electric energy cut-offs occur, or during vacation periods or for taking advantage of special energy rates. Said rechargeable battery "BAT" can be a 3-cell nickel-metal hydride (Ni-MH) battery generating a potential of 3.6 v, being able to have two or more types of recharge, a very fast recharge used when the battery "BAT" is severely discharged but it greatly shortens its service life, and normal recharge and/or battery self-discharge compensation recharge, which is slower and used when there is little consumption, for example when the battery "BAT" is at 70-80% charge, but it thus allows extending service life, reaching a service life of more than six years.

**[0031]** The device 1 can also comprise at least one temperature sensor 11, preferably an NTC type sensor, which is a thermistor performing the function of a resistive temperature sensor, and its operation is based on variation of the resistivity that a semiconductor has with temperature. Said sensor 11 is used to measure the temperature of the electrolyte 3 and sends signals 13 corre-

sponding to the measured temperature values of the electrolyte 3 to a temperature measurement interface "TMI". The signals 13 are treated in this interface "TMI" and after being treated are sent as signals 12 to the control and processing unit "CPU" so that it can identify them; the control and processing unit "CPU" processes the signals 12 received and thereby recalculates the minimum reference potential "Vminref" value. Further taking into account the time  $\Delta T$  measurements taken, together with the actuation parameters defined and set in the control and processing unit "CPU", said unit can process the data set and define the protection current "I" and the application time "Ta" for the next activation period; this definition of the protection current "I" passes as signals 7 to the direct current generator "CCG", said generator "CCG" generating the protection current "I" adapted to the external causes of corrosion, which allows establishing a potential "V" suited to the metal surface 2 to be protected.

**[0032]** The inert anode 4, which is usually an electrode made of a noble material, is used as a reference electrode, to take the potential measurements; in one embodiment, the device 1 of the invention uses an inert anode 4 made of titanium, which is measured and referenced with respect to the silver/silver chloride (Ag/AgCl) reference electrode, and for the conductivity of the electric current to be direct and for the anode to last over time, a noble metal covering, preferably a coating with a thin layer of iridium oxides and/or tantalum oxides is applied thereto.

**[0033]** Another advantage of the invention is that it reduces hydrogen  $H_2$  formation because since the method and the device of the invention maintain the metal surface 2 in an ideal protection zone and it is not excessively protected, less hydrogen is generated in the cathodic reaction on the metal surface 2 to be protected. The accumulation of hydrogen sulfide  $H_2S$  producing anaerobic bacteria (which neither live nor proliferate in the presence of oxygen) which reduce the sulfates present in potable water thereby notably decreases as hydrogen formation is reduced; therefore the final effect is that the bad odor is removed from the water.

## Claims

1. A method for impressed current anti-corrosion cathodic protection for metal surfaces (2) in contact with an electrolyte (3) with the aid of an external protection current (I), particularly for hot water accumulator tanks, in which is used an inert anode (4) acting as a reference electrode and as an anode of the protection current (I), wherein the protection current (I) is connected in activation periods (Pa) and disconnected in disconnection periods (Pd), each disconnection period (Pd) comprising a standby phase (Ps), and a measurement and regulation phase (Pmr) after the standby phase (Ps), in which a po-

tential difference  $\Delta V$  between a potential ( $V_o$ ) existing between the inert anode (4), acting as a reference electrode, and the metal surface (2) is measured, and a minimum reference protection potential ( $V_{minref}$ ) of the metal surface (2) is measured, **characterized in that** in the measurement and regulation phase (Pmr) the time  $\Delta T$  elapsing between an instant ( $t_o$ ) in which the potential ( $V_o$ ) is measured and an instant (t) in which the minimum reference protection potential ( $V_{minref}$ ) of the metal surface (2) is reached is measured, and the magnitude of the protection current (I) and an activation time ( $T_a$ ) of the next activation period (Pa) is established depending on potential difference  $\Delta V$  and time  $\Delta T$ .

2. The method according to the preceding claim, wherein if the potential difference  $\Delta V$  is greater than zero, an increment of the protection current (I) and a predefined minimum activation time ( $T_a$ ) is established for the next activation period (Pa) to then take a new measurement of the potential difference  $\Delta V$  and time difference  $\Delta T$  in the next measurement and regulation phase (Pmr).

3. The method according to claim 2, wherein if the potential difference  $\Delta V$  is less than zero and the time difference  $\Delta T$  has a value less than a predefined lower threshold time ( $t_1$ ), an increment of the protection current (I) and a predefined minimum activation time ( $T_a$ ) is established for the next activation period (Pa).

4. The method according to claim 3, wherein if the potential difference  $\Delta V$  is less than zero and the time difference  $\Delta T$  has a value greater than a predefined higher threshold time ( $t_2$ ), a reduction of the protection current (I) and a predefined minimum activation time ( $T_a$ ) is established for the next activation period (Pa).

5. The method according to claim 4, wherein if the potential difference  $\Delta V$  is less than zero and the time difference  $\Delta T$  has a value greater than the predefined lower threshold time ( $t_1$ ) and less than the predefined higher threshold time ( $t_2$ ), said time  $\Delta T$  being less than a predefined reference time ( $t_r$ ), an increase of the activation time ( $T_a$ ) is established and the protection current (I) is maintained for the next activation period (Pa).

6. The method according to claim 5, wherein if the potential difference ( $\Delta V$ ) is less than zero and the time  $\Delta T$  has a value greater than the predefined lower threshold time ( $t_1$ ) and less than the predefined higher threshold time ( $t_2$ ), said time  $\Delta T$  being greater than the predefined reference time ( $t_r$ ), a decrease of the protection current (I) is established and the activation time ( $T_a$ ) is maintained for the next activation period (Pa).

7. The method according to any of claims 1 to 6, wherein the temperature measured in the electrolyte (3) is used to correct the minimum reference protection potential ( $V_{minref}$ ) of the metal surface (2) in the measurement and regulation phases (Pmr). 5
8. A device suitable for implementing a method for impressed current anti-corrosion cathodic protection according to any of the preceding claims, comprising the inert anode (4) acting as a reference electrode and as an anode of the protection current (I), and a control and regulation unit (5) measuring the potential difference  $\Delta V$  produced between the potential ( $V_o$ ) existing between the inert anode (4), acting as a reference electrode, and the metal surface (2) when the protection current (I) is interrupted, and a minimum reference protection potential ( $V_{minref}$ ) of the metal surface (2) set in the control and regulation unit (5), **characterized in that** said device (1) progressively adapts to the causes producing corrosion, the control and regulation unit (5) measuring the time  $\Delta T$  elapsing between the instant ( $t_o$ ) in which the potential ( $V_o$ ) is measured and the instant (t) in which the minimum reference protection potential ( $V_{minref}$ ) of the metal surface (2) is reached, and said control and regulation unit (5) establishing the magnitude of the protection current (I) and the activation time ( $T_a$ ) of the next activation period (Pa) depending on the potential difference  $\Delta V$  and time  $\Delta T$ . 10  
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9. The device according to the preceding claim, wherein the control and regulation unit (5) comprises a control and processing unit (CPU) receiving input signals (6), processing them and emitting output signals (7), a potential measurement interface (PMI) receiving potential signals (8) from the inert anode (4) when it acts as a reference electrode, and sending the input signals (6) to the control and processing unit (CPU) after treating them, a direct current generator (CCG) receiving the output signals (7) from the control and processing unit (CPU), and generating the protection current (I) sending it to the inert anode (4), and a power manager (9) comprising an electric energy interface (EEI) connected to the electrical grid (10), supplying energy to the control and processing unit (CPU). 35  
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10. The device according to the preceding claim, wherein the power manager (9) also comprises a rechargeable battery (BAT) supplied by the electric energy interface (EEI) and which can replace said interface. 50
11. The device according to any of claims 8 to 10, comprising at least one temperature sensor (11), preferably an NTC temperature sensor, to measure the temperature of the electrolyte (3), said sensor (11) sending temperature signals (13) to a temperature measurement interface (TMI), which treats said signals (13) and sends signals (12) to the control and processing unit (CPU), the control and processing unit (CPU) correcting the minimum reference protection potential ( $V_{minref}$ ) of the metal surface (2) depending on the temperature signals (12) received. 55
12. The device according to any of claims 8 to 11, wherein the inert anode (4) is preferably made of titanium with a noble metal covering.



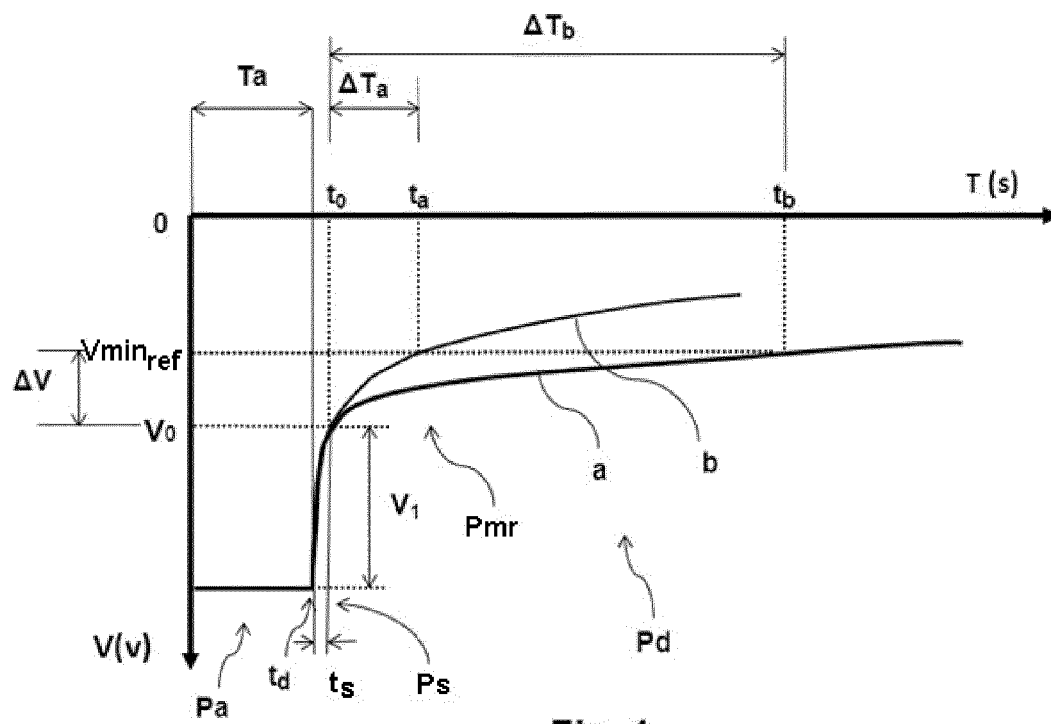


Fig. 1

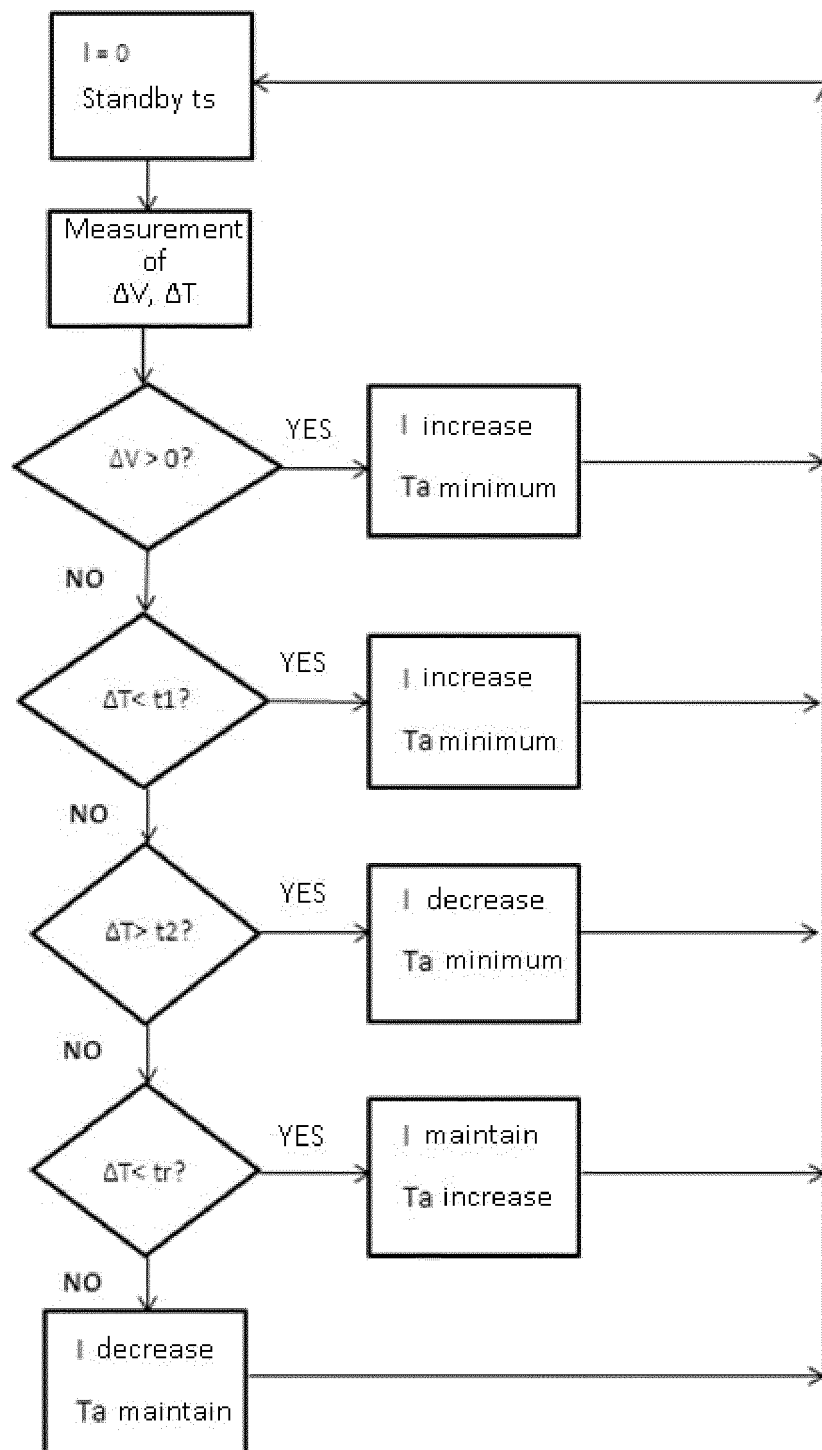


Fig. 2

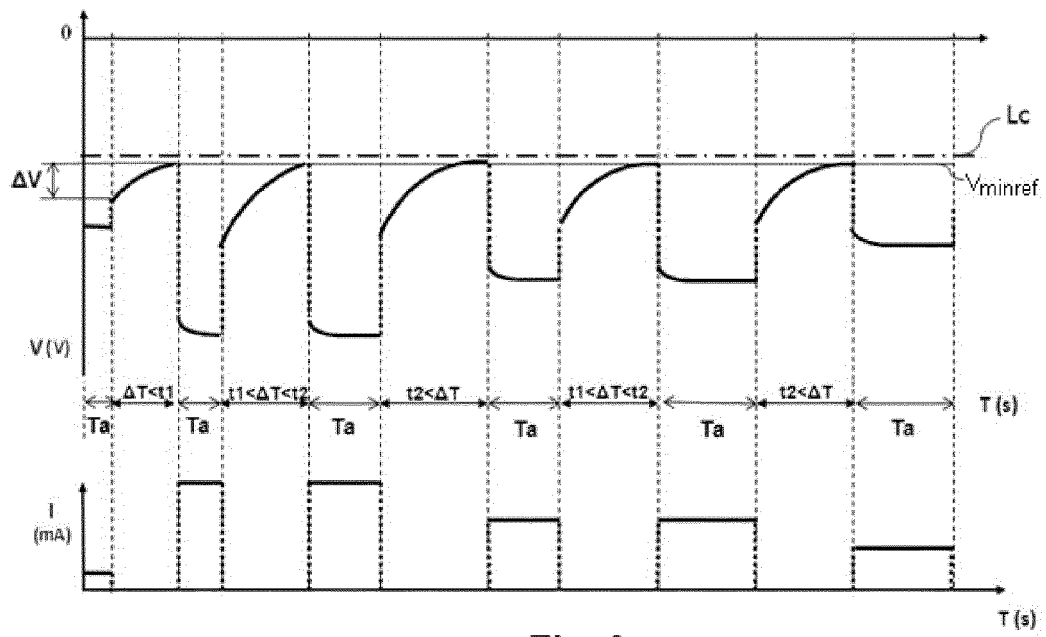


Fig. 3

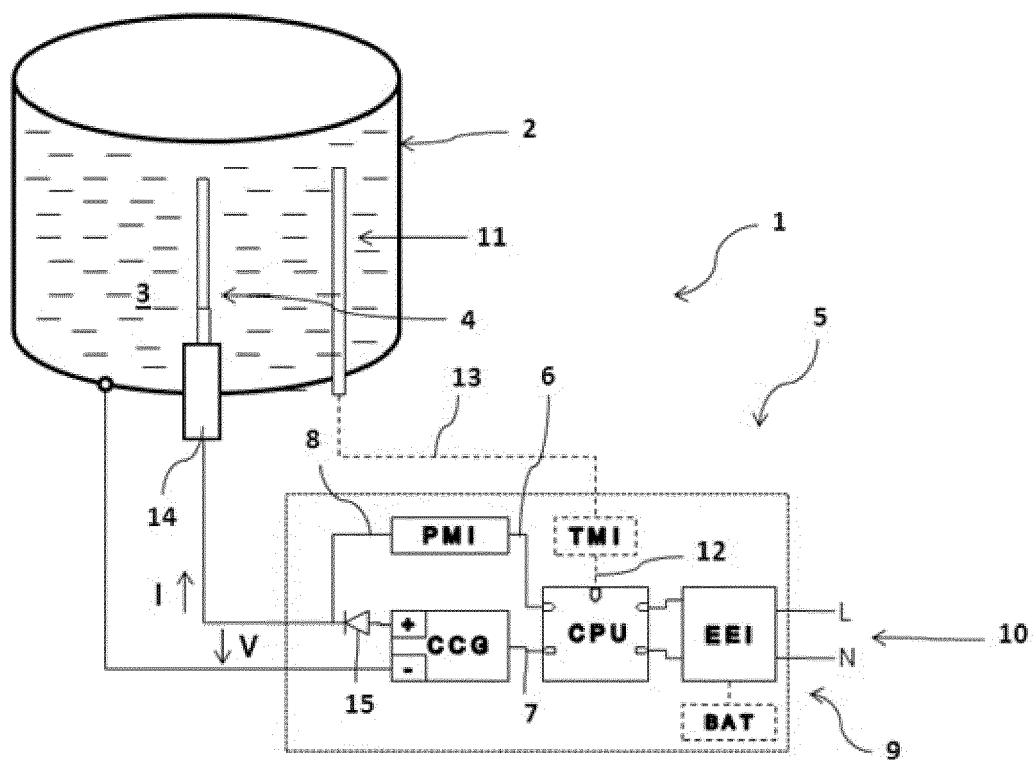


Fig. 4

**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- ES 2020584 B3 [0004]