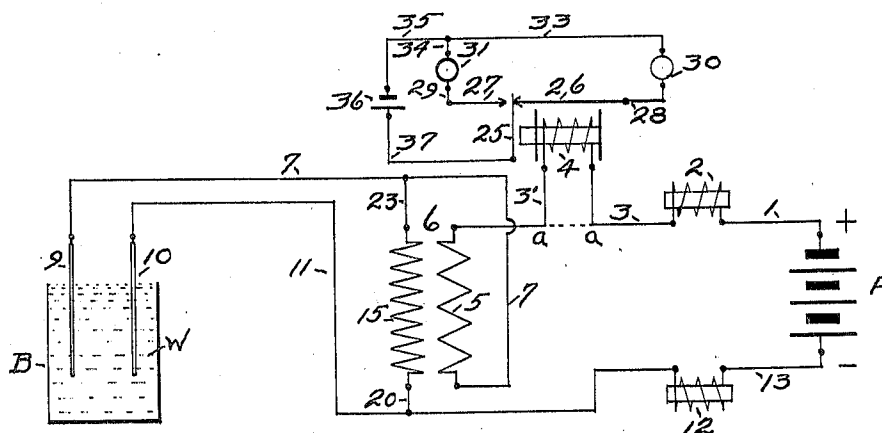
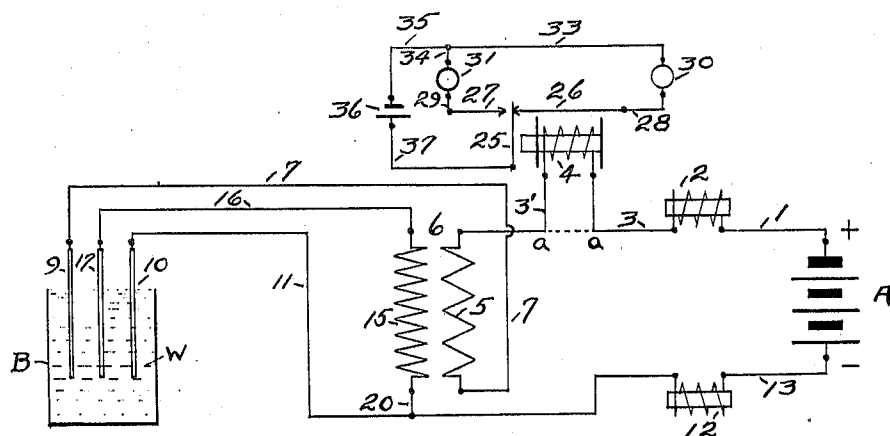


ELECTROLYTIC APPARATUS AND METHOD OF DEPOLARIZING THE SAME.

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Inventor

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## UNITED STATES PATENT OFFICE.

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ELECTROLYTIC APPARATUS AND METHOD OF DEPOLARIZING THE SAME.

Application filed April 21, 1920, Serial No. 375,502. Renewed November 5, 1921. Serial No. 513,211.

*To all whom it may concern:*

Be it known that I, WALTER DANIEL NICKUM, a citizen of the United States of America, and a resident of Glendale, in the county of Los Angeles and State of California, have invented or discovered a new and useful Improvement in Electrolytic Apparatus and Methods of Depolarizing the Same, of which the following is a specification.

This invention relates to apparatus comprising electrolytic means wherein it is desired to maintain a current of substantially uniform strength. It is an improvement on and supplements the invention disclosed in application Serial No. 275,860, filed February 8th, 1919.

An important object of the present invention is to avoid and overcome difficulties which have been found to arise in apparatus of this class by reason of so-called "polarization" and the formation of an insulating gas film at the circuit controlling electrodes, causing decrease or even practical cessation of the operating current under conditions at which the current should be maintained at full strength.

When plates of two dissimilar metals are partially immersed in a vessel containing an acidulated solution, and their outer ends are connected together by a conducting wire, an electric current is set up, caused by the acid in the solution attacking the metal plates. The water of the solution is also acted upon and free oxygen and hydrogen gases are liberated. The gases collect on the metal plates, partially adhering thereto, and form a film of very high electrical resistance, causing a rapid decrease if not an actual stoppage of the electrical action. This effect of polarization is a well known action in practically all chemical batteries.

It is also well known that when an electric current is caused to pass through an acidulated solution between electrodes immersed therein, a deterrent film of gas is formed on the electrodes due to the electrolysis of the water, and as these gases are poor conductors, the current is practically stopped. If an inductance, consisting of a coil of wire wound around a soft iron core is included in the circuit between the source of current and one of the electrodes, and if the area of said electrode, or of the electrolyte itself exposed to the action of the cur-

rent is sufficiently small, a rapid interruption of the current flowing through the circuit will take place, due to the induced extra current disrupting the gas film forming on the electrode. This forming and disrupting of the gas film is very rapid and has been taken advantage of in designing certain well known types of electrolytic interrupters, but has the disadvantage of being of little value on currents having a potential of less than 40 or 50 volts.

The present invention provides a method of maintaining a constant flow of low voltage current between plates or electrodes immersed in water or other electrolyte, by constantly reducing and practically dissipating the deterrent gas film formed by the electrolysis of the water. This is effected by taking advantage of the relatively higher voltage inverse and direct currents induced in the secondary winding of inductions coils or transformers when the primary current is varied by polarization or gas film formation to break down the gas film.

The object of the present invention is not to produce rapid interruptions in the circuit or to prevent electrolysis, but is to increase the flow of the direct current through a circuit, including an electrolytic cell, by reducing the internal resistance of the cell caused by polarization and insulating gas film formation.

With electrodes of appreciable size, it is doubtful if the flow of a current through a circuit containing an electrolytic cell is even entirely stopped. But the resistance of the gas film surrounding the electrodes, and the retarding effect of the inverse current of polarization will quickly reduce the value of the original or primary exciting current through the circuit to a minimum. It is, therefore, evident that with a given E. M. F., if the resistance of the gas film and the retarding effect of polarization can be materially reduced, then a current strength of greater constant value can be maintained. In other words, by reducing or preventing the effects of electrolysis, a current of given minimum value may be indefinitely maintained through a circuit (other factors being equal) with less E. M. F. than is possible when polarization and gas film resistance are effective.

It is not thought necessary to enter into a theoretical discussion of what actually takes

place in an electrolytic cell when a direct or unidirectional current flows through it, as the action will vary according to the composition of the electrodes and the electrolyte. It will, therefore, be assumed that the primary effect of a current flowing from one electrode to another through an electrolyte, is to alter the chemical composition of the solution by electrolysis. This, in turn produces the condition known as polarization, and under certain conditions, a gas film of high insulating quality also forms on the electrodes. It is only this condition of polarization and gas film formation, and not the actual phenomenon of electrolysis that is of present interest in this invention.

Polarization may be defined as: the production of a secondary current in a cell, contrary in direction to the principle or exciting current, due to the chemical change in the elements composing the cell. Theoretically, this is caused by the liberation of ions which collect and adhere to the respective electrodes according to polarity. An unstable chemical and electrical condition is the result, which in an attempt to neutralize itself, creates the inverse or counter-current of polarization. The strength and resistance effect against the original current is proportional to the rapidity and volumes in which the ions are liberated.

The second effect: that of the formation of an insulating gas film on the electrodes may be and probably is a direct result of the action of electrolysis. It is also possible that the counter-current of polarization may have some effect on the formation of the gas film as the nature of these gases depend upon the composition of the electrolyte, as well as that of the electrodes. It will be assumed that the electrolyte is a simple saline or acidulated solution, and that the electrodes are of some element (such as carbon) having practically no chemical reaction with the electrolyte. The gases liberated will then be composed chiefly of oxygen and hydrogen, and will adhere to their respective anode and cathode electrodes and form a film of high electrical resistance, rapidly increasing the internal resistance of the electrolytic cell to the flow of the original current.

The question as to whether the particles forming the gas film are actually the ions of polarization or a separate product of electrolysis, will not be entered into. Either or both conditions create a resistance to, or a retarding action against the flow of the original current, and will, under suitable conditions, apparently stop its flow entirely. That this interruption or stoppage of the current is not limited to cells having electrodes of small surface area exposed to the electrolyte, is illustrated by the action of certain types of electrolytic condensers,

wherein with electrodes of very large surface area and using a potential of nearly 100 volts, the flow of current is almost instantly interrupted.

When an electrolytic cell is connected to a source of direct current and the electrodes are examined with the aid of a magnifying glass, it will be noted that bubbles of gas do not immediately form on the surface of the electrodes in contact with the electrolyte. At first no action can be detected, then a whitish and more or less opaque film forms on the electrodes, first on the cathode and then on the anode. After the film appears, bubbles of gas form on the film, usually in groups, and, if the exposed surfaces of the electrodes are vertically inclined, a portion of the bubbles will break away and rise to the surface of the electrolyte. This forming and rising of the bubbles quickly reaches a maximum quantity and volume depending on the voltage employed and the electrode area in contact with the electrolyte. The quantity of bubbles thrown off increases very rapidly with an increase in voltage and vice versa, but the number adhering to the opaque film (per unit area of electrode surface) remains nearly constant, irrespective of the voltage employed. The time interval between connecting the current to the cell and the maximum rise of the bubbles is very short, seldom exceeding two or three seconds, and is less as the E. M. F. of the exciting current is greater. The needle of a galvanometer included in the circuit, will, during this period, show a very marked decrease deflection, and after a few seconds will indicate a fairly constant minimum current flow.

When the circuit is broken, the gas bubbles thrown off will slowly reduce in volume, but after they have ceased to rise, a number will still remain and adhere with the opaque film to the surface of the electrodes for an indefinite time. Again establishing the current flow, the bubbles immediately rise in maximum quantity and the galvanometer needle will register the minimum current value.

If the battery is disconnected from the cell and the outer terminals of the electrodes connected together or "shorted," the bubbles will immediately cease to rise and the opaque film with the bubbles adhering thereto will disappear in a spray or shower of fine bubbles. Removing the "short" and connecting the battery, the three stages of action will again take place, while the galvanometer will also register the same variations as first noted. Quickly reversing the direction of the current through the cell, will produce the same action as above illustrated. Suddenly increasing the E. M. F. in the same direction through the cell has the same effect, and the bubbles at first

spring outward from the surface of the electrodes in a fine shower, then begin to rise in increased volume according to voltage.

When the circuit is disconnected from the battery and "short circuited" so as to include the galvanometer, the needle will be sharply deflected in an opposite direction, indicating a decided current flow from the electrolytic cell. After the maximum deflection the needle will not return to zero; but will indicate a certain minimum current value, depending upon the length of time the exciting current has been flowing through the cell. This counter current from the electrolytic cell will gradually decrease in value, but a considerable time interval intervenes before the needle returns to the zero point. If the electrodes are brought into contact with each other under the electrolyte, or are removed and exposed to the air for a few minutes, upon removing the contact or again immersing in the electrolyte, the slowly dissipating current remaining in the cell is destroyed, and the galvanometer needle will rest at the zero point.

From the foregoing it is evident that a counter current of considerable value is set up within the electrolytic cell, and that the cell acts in the nature of a condenser of large capacity, depending upon the area of the electrodes exposed to the electrolyte. This counter current has considerable effect in retarding the flow of the original or exciting current, and coupled with the insulating qualities of the gas film, quickly reduces the original current to a minimum value.

In the induction coil, the strength of the induced secondary currents, with a given E. M. F., is directly proportional to the increased turn ratio of the secondary winding as compared to the turns in the primary. The E. M. F. value of the induced secondary currents is greater when the current flowing through the primary is broken or reduced in strength than when contact is made or the current increased. That complete interruptions of the exciting current through the primary are not necessary, but that any variation of current strength will induce secondary currents of relatively higher E. M. F., is illustrated by the well-known example of the telephone transmitter or microphone, when used in connection with an induction coil.

In the electrolytic cell, it is not necessary for complete polarization to take place, or the surface of the electrode exposed to the electrolyte to become entirely insulated by the gas film or bubbles. Theoretically, the formation of any bubble on the surface of the electrode will cause a decrease in the area of the electrode exposed to the electrolyte, and, therefore, an increase in the internal resistance of the cell with a corresponding decrease in the current flowing

through the primary winding of an induction coil included in the circuit. An induced current will, therefore, be excited in the secondary winding, having an E. M. F. value in direct proportion to the winding ratio between the two coils.

As the bubbles of gas do not form slowly and not singly, but spontaneously and in groups covering an appreciable area of the electrode surface, it is evident that current variations of considerable inductive value are produced in the primary winding, and that corresponding currents of comparatively large magnitude are induced in the secondary, and of sufficiently high E. M. F., that when properly applied to the polarized electrodes, will disrupt and expell the gas particles. In a condenser, the charge does not localize itself to any one part of the plate, but spreads over the entire area. So also in the electrolytic cell under discussion, the induced current acts over the entire exposed surface area of the electrode, disrupting or repelling any of the gas particles adhering thereto.

The accompanying drawings illustrate embodiments of my invention, and referring thereto:

Figure 1 is a diagram illustrating the principle involved in overcoming polarization.

Figure 2 is a diagram showing a modified form of the circuits.

For the purpose of illustration, I have shown in Figs. 1 and 2, the application of the invention in depolarizing an electrolytic device constituting a circuit controller for an electromagnet coil 4 whose armature 25 controls a circuit, such as a signal circuit. Electro-magnet 4 is simply typical of a translating device of some kind included in the circuit, and any other translating device may be substituted therefor, according to the specific application of the invention, or in some cases, as hereinafter explained, this translating device may be omitted. In the specific application of the invention as illustrated in the drawings, the electro-magnet 4 may act as a relay for controlling a signal circuit, for example, the armature 25 of said electromagnet having front contact 26 and back contact 27, respectively connected by wires 28 and 29 to suitable signal means or other translating devices, such as 30 and 31 from which wires 33 and 34 lead to wires 35 connected to one side of battery 36, and whose other side is connected by wire 37 to armature 25. With this arrangement the armature 25 will close one or the other of the branch circuits through the respective devices 30 and 31 according to the condition of energization or de-energization of the circuit through the electrolytic device comprising the electrolyte W and the electrodes immersed therein, and in this application of

the invention the main object thereof is to enable continuous energization of this circuit, without interference by polarization effects.

5 A particular application of the invention is claimed specifically in application Serial No. 254,345, filed Sept. 16th, 1918, of which application Serial No. 275,860, filed Feb. 8th, 1919, is a division and of which this appli-  
10 cation is an improvement. The present application relates to the broad process and improved means for applying the apparatus for depolarization.

Referring to Figure 1, which illustrates  
15 the circuits as far as is required for explaining the depolarizing action, the battery A is shown as connected in a circuit including a wire 1 leading from said battery to an impedance or choke coil 2 from which a wire  
20 3 leads to an electromagnet coil 4, a primary winding 5 of a transformer 6 being also included in this connection by means of the wire 3'. From said primary winding a wire 7 leads to an electrode 9 immersed in an elec-  
25 trolite, such as a body W of water, or dilute acid, or alkaline or neutral salt solution contained in a vessel B. From another electrode 10 immersed in such a liquid, a wire 11 leads to an impedance or choke coil 12  
30 from which a wire 13 leads back to battery A. A secondary winding 15 of transformer 6 is connected at one end to wire 7 by wire 23 and at the other end by wire 20 to wire 11.

If current is allowed to flow from the positive side of battery A through wire 1, impedance coil 2, wire 3, relay coil 4, wire 3', primary winding 5 and wire 7, to electrode 9, through solution W in vessel B to electrode 10 and wire 11, impedance coil 12, and  
40 wire 13, back to negative side of battery A, the water in the solution W will be more or less decomposed by the current passing through it and gas will collect on the electrodes, the degree of electrolysis of the water  
45 depending upon the quantity of current flowing through the circuit. The gases liberated by the decomposition of the water and collecting on the electrodes in the solution W, as heretofore mentioned, quickly reduce the  
50 flow of current.

As the secondary winding 15 of transformer 6 is connected in parallel or bridged across the circuit, a portion of the battery current will be shunted through said secondary winding 15, its value depending upon  
55 the resistance of the coil. The primary 5 and secondary 15 of transformer 6 are connected to the circuit in such an inductive relation that the momentary induced secondary current generated when the current  
60 flow is first established will flow in a direction and through that part of the circuit indicated by wire 23, wire 7, electrode 9, solution W, electrode 10, wire 11 and wire 20.

65 But, as the induced current generated in a

secondary winding at the "make" of a circuit connection is comparatively feeble, the said induced current generated in secondary 15 will be partly if not entirely neutralized by the primary current shunted through 70 said secondary winding 15.

The primary or exciting current rapidly reaches its maximum current flow, but, due to the counter current of polarization and the insulating gas film set up in the electrolytic cell by the electrolysis of the solution, a more or less rapid drop in value of the primary current immediately follows. As the lines of force generated in the primary winding 5 collapse, a relatively high voltage induced current is generated in the secondary winding 15, and will flow in a direction and through that part of the circuit indicated by wire 20, wire 11, electrode 10, solution W, electrode 9, wire 7 and wire 23, 85 and will disrupt the gas particles adhering to the electrodes and particularly those on electrode 10, and as these gas particles carry an electrical charge opposite in sign to the polarity of the electrode upon which they 90 collect, and, as the induced secondary current flows in a direction through the cell opposite to the original exciting current, and is of a polarity of like sign to the charged gas particles, said gas particles will be repelled away from their respective electrodes, as well as disrupted by the said secondary current. The condenser current in the cell (as heretofore illustrated) will also have a tendency to flow through the circuit and in a 100 direction indicated by electrode 9, wire 7, wire 23, secondary winding 15, wire 20, wire 11, electrode 10, and solution W to electrode 9. This condenser current will exalt the secondary current and also dissipate the 105 counter current of polarization. Immediately on the dissipating of the gas film and the counter current of polarization the primary current again rapidly increases in value until checked by polarization and gas 110 film formation, when the operation above described is repeated.

It is therefore evident that a more or less complete cycle of oscillations are set up in that part of the circuit comprising the electrolytic cell and the secondary winding 15, and that these oscillations are sufficiently rapid to materially reduce the retarding effects of polarization and gas film formation on the primary current flowing through the 120 electrolytic cell, which will therefore have a higher value than if polarization and insulating gas film formation were effective, so that an almost constant flow of direct current will be maintained through the primary circuit, and the relay 4 or other device in the circuit will be constantly energized as long as the electrode plates 9 and 10 are immersed in the solution W.

As the secondary coil 15 of transformer 6 130

is practically bridged across the circuit, and as the induced current generated in said secondary coil becomes practically alternating in character, and to prevent any loss of its efficiency in acting upon the gas film on the electrodes by a certain portion of the secondary current backing up through the battery A, the impedance or choke coils 2 and 12 are introduced in the circuit to impede the transmission of any such alternating current through that part of the circuit which includes the battery A.

The winding of the secondary coil 15 must be so proportioned that it will have a resistance equal to or greater than the total resistance of the primary circuit, and the relay coil 4 must be so designed that it will not be sufficiently energized by the small amount of current flowing through the secondary coil 15 to hold the armature 25 thereof when the primary circuit has been opened by removing one or both of the electrode plates 9 and 10 from the solution W, or when the plates have been so removed and the primary circuit disconnected from the battery A that the coil of the relay will not be sufficiently energized to attract its armature when the battery A is again connected, until the total resistance has been reduced by again immersing the electrodes 9 and 10 in the solution W.

It is evident from the foregoing that other electrically operated apparatus could be introduced in the primary circuit besides the relay coil 4, or that said relay can be dispensed with by making direct connection between the wires 3 and 3', as shown in the dotted lines at "a-a," if it is desired to use the depolarizing effect of the secondary circuit to maintain a flow of low voltage direct current through the solution W for the purpose of electrolysis. For instance, certain applications in chemistry and electro-metallurgy whereby desired actions could be obtained with low voltage that could not be obtained with greater voltages, as for instance, the so-called burning effect of too high voltage in electro-plating, also the purification of water or sewage. In any such application of the invention the electrodes 9 and 10 may constitute the electrodes of the electrolytic cell to which the depolarizing circuit is applied.

An equally effective circuit arrangement for some purposes is shown in Figure 2, where for mechanical or electrical reasons, it is not desirable to simplify the construction of apparatus containing the electrodes by reducing their number or the number of wires leading thereto. A third electrode plate 17 is immersed in the solution W in vessel B, and in a more or less close relation to electrode 10, said electrode 17 being connected by the wire 16 to secondary winding 15 of transformer 6. The other side of sec-

ondary 15 being connected by wire 20 and wire 11 to electrode 10, as in Figure 1. With this circuit arrangement the depolarizing and gas film disrupting effects of the induced secondary current will be localized on the electrode plate 10. The circuit arrangement of Fig. 2, is of special value in certain types of electrolytic devices, as for instance the aforementioned electro-plating bath, wherein the depolarizing induced currents could be localized and concentrated on the cathode. The operation of the circuit in Figure 2 is substantially the same as described for Fig. 1.

It will be understood that the operation of this invention does not require complete interruption of the current by the depolarizing action, it being required only that there shall be a sufficient decrease or variation of the current to produce the required inductive effect in the secondary circuit to dissipate the condition of polarization and insulating gas film.

What I claim is:

1. In an electrical depolarizing apparatus comprising a circuit including a source of direct current and electrodes in contact with an electrolyte, means for maintaining the current effectiveness of said circuit consisting of a transformer having a low tension primary winding in series with and energized by said circuit, and a high tension secondary winding in electrical connection with said electrodes and inductively related to said primary winding in such a manner as to cause a reduction of polarization between said electrodes and said electrolyte when the current in the primary winding is varied by said polarization.

2. In an electrical depolarizing apparatus comprising a circuit including a source of direct current and electrodes in contact with an electrolyte, a transformer having a low tension primary winding in series with and energized by said circuit and a high tension secondary winding in electrical connection with said electrodes and inductively related to said primary winding in such a manner as to dissipate a condition of polarization between said electrodes and said electrolyte, and disrupt a condition of insulating gas film formation occurring on said electrodes and produced by the current acting on said electrolyte, when the current in said primary winding is varied or reduced by said polarization and said insulating gas film formation.

3. In an electrical depolarizing apparatus comprising a circuit including a source of direct current and electrodes in contact with an electrolyte, a transformer having a low tension primary winding in series with and energized by said circuit, and a high tension secondary winding electrically connected to said electrodes, and inductively related to

said primary winding in such a manner as to dissipate a condition of polarization and insulating gas film formation on said electrodes, and impedance coils between said source of current and said transformer secondary coil.

4. In an electrical depolarizing apparatus comprising a circuit including a source of direct current and electrodes in contact with an electrolyte, a transformer having a low tension primary winding in series with and energized by said circuit, and a high tension secondary winding bridged across said circuit and electrically connected to said electrodes and inductively related to said primary winding in such a manner that induced inverse and direct secondary currents will be generated in said secondary winding during variations in the current in said primary winding produced by a condition of polarization and insulating gas film formation on said electrodes, and directionally applying said inverse and direct induced currents to said electrodes to dissipate the said condition of polarization and to disrupt and repel the said insulating gas film formation from said electrodes.

5. In an electrical depolarizing apparatus comprising a circuit including a source of direct current and electrodes in contact with an electrolyte, a transformer having a low tension primary winding in series with and energized by said circuit, and a high tension secondary winding bridged across said circuit and electrically connected to said electrodes, and in inductive relation with said primary winding in such a manner as to dissipate a condition of polarization and insulating gas film formation on said electrodes, and impedance coils between said source of current and said secondary winding, and said secondary winding having a resistance equal to or greater than the resistance of the circuit through the electrodes and the electrolyte.

6. In an electrical apparatus comprising a circuit including a source of direct current and circuit controlling electrodes in contact with an electrolyte and positioned to break contact therewith; and an electromagnet relay also included in said circuit and having circuit controlling contacts controlled thereby, and a transformer having a low tension primary winding in series with said circuit and energized thereby, and a high tension secondary winding electrically con-

nected to said electrodes and inductively related to said primary winding in such a manner as to maintain the current effectiveness through said circuit when said electrodes are immersed in said electrolyte by dissipating a condition of polarization and insulating gas film formation produced on said electrodes by said current acting on said electrolyte.

7. In an electrical depolarizing apparatus comprising a circuit including a source of direct current and electrodes immersed in an electrolyte, a transformer having a low tension primary winding in series with and energized by said circuit, and a high tension secondary winding inductively related to said primary winding and in electrical connection with one of said electrodes and a third electrode also immersed in said electrolyte in such a manner as to reduce a condition of polarization between said electrodes when said primary current is varied or reduced by said polarization.

8. In an electrical depolarizing apparatus comprising a circuit including a source of direct current and electrodes immersed in an electrolyte, a transformer having a low tension primary winding in series with and energized by said circuit and a high tension secondary winding inductively related to said primary winding and in electrical connection with one of said electrodes and a third electrode also immersed in said electrolyte in such a manner as to localize on one of said first named electrodes the depolarizing and gas film disrupting effects of the inverse and direct induced currents generated in said secondary winding when the primary current is varied or reduced by polarization or insulating gas film formation produced on said electrodes by said current acting on said electrolyte.

9. The method of depolarizing surfaces exposed to an electrolyte and included in part of an electric circuit, which consists in causing the current variations in said circuit due to polarization and insulating gas film formation to induce momentary inverse and direct induced currents of relatively high tension and predetermined polarity and applying such high tension and polarized currents to the polarized and gas film insulated surfaces to depolarize the same and disrupt the gas film formation.

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