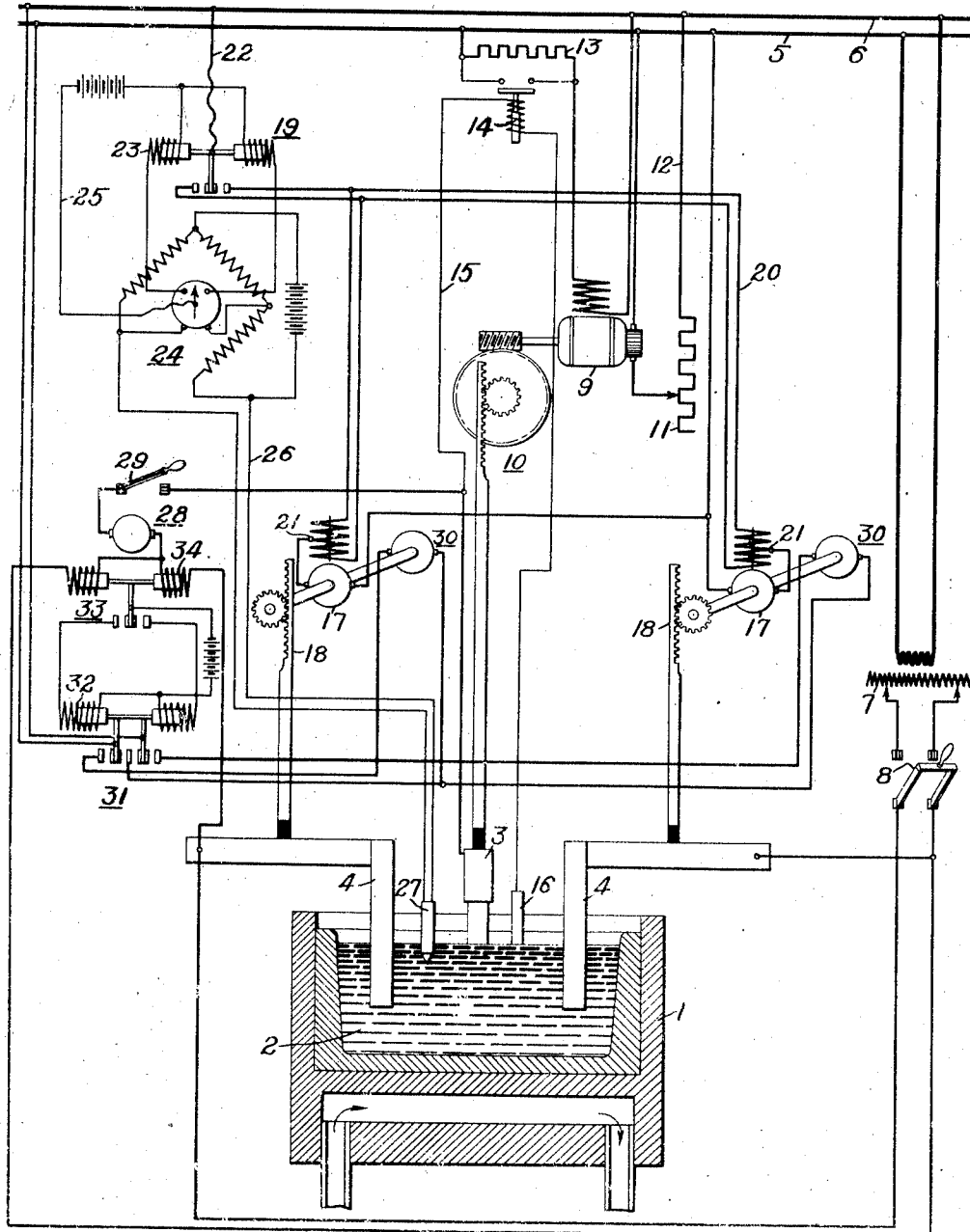


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 AUTOMATIC OPERATION OF ELECTROLYTIC CELLS.
 APPLICATION FILED NOV. 20, 1919.

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Patented Nov. 15, 1921.



WITNESSES:

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AUTOMATIC OPERATION OF ELECTROLYTIC CELLS.

1,396,919.

Specification of Letters Patent.

Patented Nov. 15, 1921.

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To all whom it may concern:

Be it known that I, PORTER H. BRACE, a citizen of the United States, and a resident of Pittsburgh, in the county of Allegheny and State of Pennsylvania, have invented a new and useful Improvement in Automatic Operation of Electrolytic Cells, of which the following is a specification.

My invention relates to electrolytic cells and, more particularly, to cells adapted to the production of metals from their fused salts, especially metals of the alkaline earth group comprising calcium, strontium and barium, and it has, for its primary object, the provision of a cell of the above designated character which shall be automatic in operation.

In the past, calcium and like metals have been prepared, electrolytically, by the employment of various types of apparatus, the most common of which has been that in which a graphite cup functions both as an anode and as a container for the electrolyte, and in which the metal has been deposited on a cathode which has been moved vertically upward as the accumulation of the metal has increased.

By this method an irregular rod of the desired metal has been produced which has varied greatly both in its diameter and in its quality because of varied conditions within the cell. It has been found that the temperature of the electrolyte is a factor of great importance and that the character of the deposit and the efficiency of the cell are greatly affected by changes in the temperature of the electrolyte. Through investigation, it has been also ascertained that the conditions at the anode are continually changing, the changes having to do with the size and position of the area on the anode over which current is passing to the electrolyte. These changes are erratic and uncontrollable and give rise to very troublesome fluctuations of electrolyte temperature.

It has been customary to compensate for these changes in electrolyte temperature by varying the current passed through the cell and the rate of movement of the cathode. Such adjustments have been unsatisfactory, however, so that even when a skilled operator is employed, the cross section of the metal deposit formed, its character as re-

gards included impurities, such as included electrolyte, and the general efficiency of the process as a whole have been subject to wide variations.

As a result, it has heretofore been impossible to secure any practical means of automatically controlling the operation of a cell, and the cost of producing metals, by electrolysis of their fused salts, has, therefore, been very high because of the necessity of constant supervision of the process by one skilled in the art.

One object of my present invention is to provide a means for securing metals, and particularly calcium and metals of like character, in the form of deposits of a high degree of uniformity both physical and chemical.

I have ascertained that the character of the deposit and, consequently, the efficiency of the cell are greatly affected by changes in the temperature of the electrolyte, and that, consequently, this temperature is a factor of great importance. Furthermore, the temperature of the electrolyte, other things being equal, is a function of the energy input of the cell.

With these discoveries in mind, a further object of my invention comprises the control of electrolyte conditions and, particularly, its temperature by varying the position of the anode or anodes, rather than that of the cathode, to thereby vary the position and size of the anode area over which current is passing to the electrolyte in such manner that a constant current may be employed. In other words, my invention comprehends the electrolysis of fused salts by the employment of a constant current and a substantially uniformly moved cathode, together with one or more anodes moved in accordance with the varying conditions of the electrolytic bath composed of the fused salts being treated.

More particularly, my invention comprehends the employment of means governed by changes in temperature of the electrolytic bath for automatically causing compensating changes in the position or positions of the anode or anodes employed in the cell.

In prior practice, during the electrolysis of fused salts, the metal being deposited upon the cathode was deposited more or less

from the direction of the current supply from the anode so that the resultant rod of metal was frequently curved or crooked.

Another feature of my invention, therefore, resides in the employment of a plurality of anodes symmetrically disposed with respect to a common cathode in order that the metal deposited may produce a substantially uniform body or rod.

In this connection, an additional feature of my invention consists in the provision of means, governed by the relative flow of current from the several anodes to the cathode, for producing minor independent variations in the automatic adjustments of the anodes, to thereby secure an equality in the flow of current from the anodes to the cathode to thus prevent the deposit on the cathode from growing toward one side or another.

While the foregoing means will render the operation of the cell substantially automatic, I have found that there are sudden and frequent variations, in the local conditions of the electrolyte about the cathode, which should be compensated for in order to obtain the best results. Another object of my invention, therefore, consists in providing means, controlled by voltage changes in the vicinity of the cathode, for correspondingly changing the rate of upward movement of the cathode. This, what may be termed secondary control of the cathode, also serves to offset the effect of lagging in response to the various other regulating means employed.

While my invention is applicable to the electrolytic production of numerous metals from their fused salts, as well as to other more general purposes, I will, for the sake of clearness, describe it as applied to the production of metallic calcium from its fused chlorid.

Reference may now be had to the single figure of the drawing, which is a diagrammatic view of an electrolytic cell and its controlling apparatus, embodying a preferred form of my invention.

In the drawing I have shown an electrolytic cell, suitable for the electrolysis of fused salts, which may comprise a cup or container 1 having a bottom which may be water-cooled if desired, and containing a fused electrolyte 2 in which a cathode 3 and a plurality of anodes 4, symmetrically disposed with respect to the cathode, are partially immersed in the usual manner.

The salt comprising the electrolytic bath may be initially fused by any suitable means. For example, supply lines 5 and 6 may lead from any suitable source of alternating current to the primary winding of a variable transformer 7, the secondary winding of which may be connected to the anodes as indicated, a switch 8 being interposed between the transformer and the anodes. By

this means, alternating current may be passed between the anodes to heat and fuse the salt forming the electrolytic bath, after which the electrolysis may be conducted, as will be later explained.

As a means for raising the cathode vertically as metal is deposited upon it, I provide a shunt-wound motor 9 which is operatively connected to the cathode by any suitable speed-reducing mechanism 10 so that the cathode will be raised at a relatively slow rate, depending upon the rate of speed of the motor. A variable, non-inductive resistor 11 is included in the armature circuit 12 of the motor while a non-inductive resistor 13 is included in the field circuit of the motor. Means including a relay 14 may be provided for shunting the resistor 13 under normal conditions and the actuating coil of this relay may be in a circuit 15 with the cathode 3 and an auxiliary electrode 16 disposed within the electrolytic bath and adjacent to the cathode.

The resistor 13, which may be inserted in the field circuit under certain conditions, provides a means for decreasing the speed of the motor 9 to decrease the speed at which the cathode is raised, as will be more fully pointed out during the description of the operation of my apparatus.

By my invention, the temperature of the electrolytic bath is controlled, mainly, by varying the position and size of the areas of the anodes from which current passes to the electrolyte and so to the cathode. This may be done by any suitable means, governed by changes in temperature of the electrolytic bath and capable of raising and lowering the anodes in proportion to the changes in temperature.

For example, I may employ, in conjunction with each anode, a shunt-wound reversible motor 17 having a suitable mechanical connection 18 with its anode. The field terminals of each motor 17 are respectively connected to the fixed contacts of a balanced relay 19 by conductors 20 while its armature winding is connected at one side to an intermediate tap 21 of the field winding and at its other side to the supply conductor 5. The movable contact member of the balanced relay 19 may be electrically connected, as at 22, to the other supply conductor 6 so that, when the one or the other of the actuating coils 23 of the relay 19 is energized, a circuit will be established through the one or the other of the opposed sections of the field winding of the motor to drive the motor in the corresponding direction.

A circuit-closing bridge galvanometer 24 has its fixed contact members connected to corresponding terminals of the actuating coils 23 and its movable contact member connected to the opposite terminals of the coils, a suitable source of electrical energy, 130

such as a battery, being included in the circuit 25 thus provided. The galvanometer is connected in a circuit 26 with a thermocouple 27 partly immersed in the electrolytic bath whereby changes in temperature in the bath will cause the galvanometer to actuate the balanced relay 19 and thus effect simultaneous operation of the motors 17.

As a means for carrying out the electrolysis of the electrolytic, I may provide any suitable source of direct current, such as a direct-current generator 28. One terminal of the generator is connected to the cathode while its other terminal is connected by branch circuits with the several anodes employed. Preferably a switch 29 is interposed in the common portion of this circuit to control the operation of the cell.

Unless the currents flowing from the several anodes to the common cathode have the same value in each instance, there will be a tendency, upon the part of the metal being deposited upon the cathode, to grow toward that anode from which the greater current flows. It is, therefore, advisable to provide means for insuring that the currents from the several anodes to the cathode have equal values.

As a means for accomplishing this, I may provide motors 30 mechanically coupled with the motors 17 to assist or oppose the latter, as the circumstance may be. One terminal of each motor 30 may be connected to a fixed contact member of a double-pole balanced relay 31 while the other terminals of the motors 30 may be connected to separate fixed contact members of the relay. The movable contact members of the relay 31 may be connected with the line conductors 5 and 6, as indicated, whereby movement of the relay in either direction will close a circuit through one or the other of the motors 30.

The relay 31 may have one terminal of each of its actuating coils 32 connected through a suitable source of energy, such as a battery, with the movable contact of a balanced relay 33 and its other terminals connected to the fixed contacts of the relay 33. The actuating coils 34 of this latter relay may be included in the branches of the circuits through the generator 28, anodes 4 and the cathode 3.

The operation of my invention may best be understood by assuming that the apparatus is in the position shown in the drawing with all switches open. A quantity of the salt to be treated is disposed within the container 1. The switch 8 is closed and the anodes are brought into contact and then separated to establish an arc which will melt portions of the cold salt between them to form a pool of molten electrolyte into which the anodes are then lowered. The molten salt then conducts the current and is rapidly

heated thereby so that additional salt may be added and melted to bring the electrolytic bath to the desired volume. The temperature of the bath may then be adjusted to the desired point by control of the heating current, after which the switch 8 may be opened and the switch 29 may be closed to establish an electrolyzing circuit including the generator, anodes and the cathode.

Preferably, the cathode may be first brought into contact with the electrolyte and then slightly separated therefrom to establish an arc which is allowed to burn a few minutes in order to heat the cathode to a temperature above the melting point of calcium in order that the metal first deposited will wet the surface of the cathode and insure good thermal and electrical contact therewith. The cathode is then again brought into contact with the electrolyte and the electrolysis is begun.

The rate of upward movement of the cathode and the value of the current passed through the electrolytic bath are then adjusted to the proper values after which the control of the cell is substantially automatic. If, at any time, the temperature of the electrolytic bath becomes too high or too low, the current generated by the thermocouple 27 will actuate the bridge galvanometer 24 to, in turn, actuate the balanced relay 19 to connect the motors 17 with the supply lines and cause them to raise the anodes if the temperature is too low or to lower them if the temperature is too high. The raising or lowering of the anodes decreases or increases the area of the anodes from which the current is passing and thus increases or decreases, as the case may be, the voltage drop between them and the cathode so as to produce an immediate rise or fall in the temperature of the electrolyte. Under normal conditions, that is, if the temperature of the cell remains constant, the balanced relay 19 will remain open and the motors 17 will be inactive.

If, for any reason, the value of the current passing from any anode to the cathode exceeds that of the current passing from another anode to the cathode, the relay 33 will become unbalanced and will consequently actuate the relay 31 to close a circuit through the corresponding supplemental motor 30 to drive the motor in such direction as to raise its anode, which is carrying the greater current, until the current between it and the cathode has been reduced to a value equal to that of the current flowing between the other anode or anodes and the cathode. By this means, any tendency of the deposited metal to grow toward one or the other of the anodes is prevented.

The foregoing regulating devices comprise the principal features of the automatic control of an electrolytic cell according to my

invention. However, although the average speed of the cathode should be substantially constant under my method of operation, yet it may be necessary to make small changes in its speed in order to compensate for sudden variations in local conditions about the cathode and to offset the effect of lag in the response of the cell to the other regulating means for controlling it.

These secondary variations in the speed of the cathode are governed by changes in voltage between the cathode and the electrolyte through the circuit including the cathode and the nearby auxiliary electrode 16. Under normal operating conditions, the current traversing this circuit holds the relay 14 in closed position to shunt the resistor 13 of the field winding of the motor 8. If, however, the voltage drop between the cathode 3 and the auxiliary electrode 16 falls below a predetermined value, the relay 14 will be correspondingly deenergized and the resistor 13 will be included in the field circuit of the motor 9 to increase the speed of the motor and thereby decrease the cathode area in contact with the electrolyte, thus causing higher current density, voltage drop and electrolyte temperature.

Through the employment of an electrolytic cell provided with the controlling apparatus illustrated and described, it is possible to secure metals, such as calcium, in the form of deposit of a high degree of uniformity, both physical and chemical. This has been possible while operating at constant current and with practically a constant rate of cathode advance and the operation of the cell may be made substantially automatic so that skilled attendance is unnecessary.

Although they form no part of my present invention, the cell may be rendered more automatic in its operation by providing one or more anodes of the character set forth in a copending application filed by me on Nov. 13, 1919, Serial No. 337,682 and assigned to the Westinghouse Electric and Manufacturing Company, in which I disclose means for replenishing the electrolyte of electrolytic cells. This may be done by providing an electrode with a chamber containing a solid body of electrolyte material which is constantly fused and passed to the electrolyte during operation of the cell. Furthermore, if desired, the temperature of the electrolytic bath may be additionally governed, within certain limits, by employing one or more cooled electrodes, as anodes, such as those disclosed in a copending application covering the temperature control of electrolytic cells filed by me on Nov. 13, 1919, Ser. No. 337,683, and assigned to the Westinghouse Electric and Manufacturing Company.

While I have illustrated a preferred embodiment of my invention and have de-

scribed it as applied to the production of calcium from a fused salt of calcium, it will be appreciated that it is applicable to electrolytic cells of various characters and for different purposes and that both its manner of employment and the details of its controlling mechanism are to be in no way limited, except as indicated in the claims.

I claim as my invention:—

1. In a control system for electrolytic cells, the combination with an electrolytic bath, a cathode and an anode, of means governed by changes in the temperature of the bath for varying the action of the anode.

2. In a control system for electrolytic cells, the combination with an electrolytic bath, a cathode and an anode, of means governed by changes in the temperature of the bath for varying the extent of immersion of the anode in the bath.

3. In a control system for electrolytic cells, the combination with an electrolytic bath, a cathode and an anode, of means operable to raise and lower the anode with respect to the bath and means controlled by the temperature of the bath for causing the operation of the first mentioned means.

4. In a control system for electrolytic cells, the combination with an electrolytic bath, a cathode and a plurality of anodes, of means governed by changes in the temperature of the bath for simultaneously raising and lowering the anodes.

5. In a control system for electrolytic cells, the combination with an electrolytic bath, a cathode and a plurality of anodes, of means governed by changes in the temperature of the bath for simultaneously raising and lowering the anodes, and means for independently accelerating or retarding the movement of the anodes.

6. In a control system for electrolytic cells, the combination with an electrolytic bath, a cathode and a plurality of anodes, of means governed by changes in the temperature of the bath for simultaneously raising and lowering the anodes, and means controlled by the relative values of the currents from the several anodes to the cathode for independently varying the raising and lowering of the several anodes.

7. In a control system for electrolytic cells, the combination with an electrolytic bath, a cathode and a plurality of anodes, of means for effecting the flow of currents from the several anodes to the cathode, and means for equalizing the currents between the several anodes and the cathode.

8. In a control system for electrolytic cells, the combination with an electrolytic bath, a cathode and a plurality of anodes, of means for effecting the flow of currents between the anodes and the cathode, means for raising and lowering the anodes to control the temperature of the bath and means for inde-

pendently retarding or accelerating the movement of the anodes to equalize the respective currents passing between them and the cathode.

5 9. In a control system for electrolytic cells, the combination with an electrolytic bath, a cathode and an anode, of means for connecting the several anodes and the cathode in an electrolyzing circuit, means governed by the
10 temperature of the bath for simultaneously raising and lowering the anodes, and means governed by the relative values of the currents between the several anodes and the cathode for independently raising the anodes.

15 10. In a control system for electrolytic cells, the combination with an electrolytic bath, of a cathode, means for normally raising the cathode at a uniform speed, and means controlled by voltage conditions in the
20 electrolytic bath adjacent to the cathode for accelerating its rate of movement under certain conditions.

25 11. In a control system for electrolytic cells, the combination with an electrolytic bath, an anode, a cathode, and means for effecting a flow of current between the anode and cathode through the bath, of means for normally raising the cathode at a predetermined speed and means operable when the
30 voltage drop in the electrolyte adjacent to the cathode falls below a predetermined value for accelerating the raising of the cathode.

35 12. In a control system for electrolytic cells, the combination with an electrolytic bath, a cathode, a plurality of anodes, and means for effecting a flow of current from the several anodes to the cathode, of means for normally raising the cathode at a pre-
40 determined rate, and means governed by the temperature of the electrolyte for raising and lowering the anodes.

45 13. In a control system for electrolytic cells, the combination with an electrolytic bath, a cathode, a plurality of anodes, and means for effecting the flow of currents from the several anodes to the cathode, of means for normally raising the cathode at a
50 predetermined rate, means governed by the temperature of the electrolyte for raising and lowering the anodes, and means controlled by the value of the currents between the several anodes and the cathode for equal-
55 izing the currents between the anodes and the cathode.

14. In a control system for electrolytic cells, the combination with an electrolytic bath, a cathode, a plurality of anodes and means for effecting the flow of currents be-
60 tween the several anodes and the cathode, of means normally acting to raise the cathode at a predetermined rate, means controlled by the temperature of the bath for simultaneously raising and lowering the anodes, and
65 means controlled by the relative values of the currents between the several anodes and the cathode for independently adjusting the anodes.

15. In a control system for electrolytic cells, the combination with an electrolytic bath, a cathode, a plurality of anodes and means for effecting the flow of currents be-
70 tween the several anodes and the cathode, of means normally acting to raise the cathode at a predetermined rate, means controlled
75 by the temperature of the bath for simultaneously raising and lowering the anodes, means controlled by the relative values of the currents between the several anodes and the cathode for independently adjusting the
80 anodes, and means operable when the voltage drop in the electrolyte adjacent to the cathode falls below a predetermined value for accelerating the raising of the cathode.

16. In an electrolytic cell operating at sub-
85 stantially constant current, the combination with one electrolyte and a vertically disposed cathode which is raised at substantially constant rate as a deposit of metal accumulates thereon, of anodes independently movable,
90 and means for moving the anodes to maintain the temperature of the electrolyte within predetermined limits.

17. In an electrolytic cell operating at sub-
95 stantially constant current, the combination with an electrolyte bath and a vertically disposed cathode which is raised at a substantially constant rate as a deposit of metal accumulates thereon, of anodes independ-
100 ently movable, means for moving the anodes to maintain the temperature of the electrolyte within predetermined limits, and means for accelerating the movement of the cathode
105 when the voltage drop in the bath adjacent to the cathode falls below a predetermined value.

In testimony whereof, I have hereunto subscribed my name this 29th day of October, 1919.

PORTER H. BRACE.