

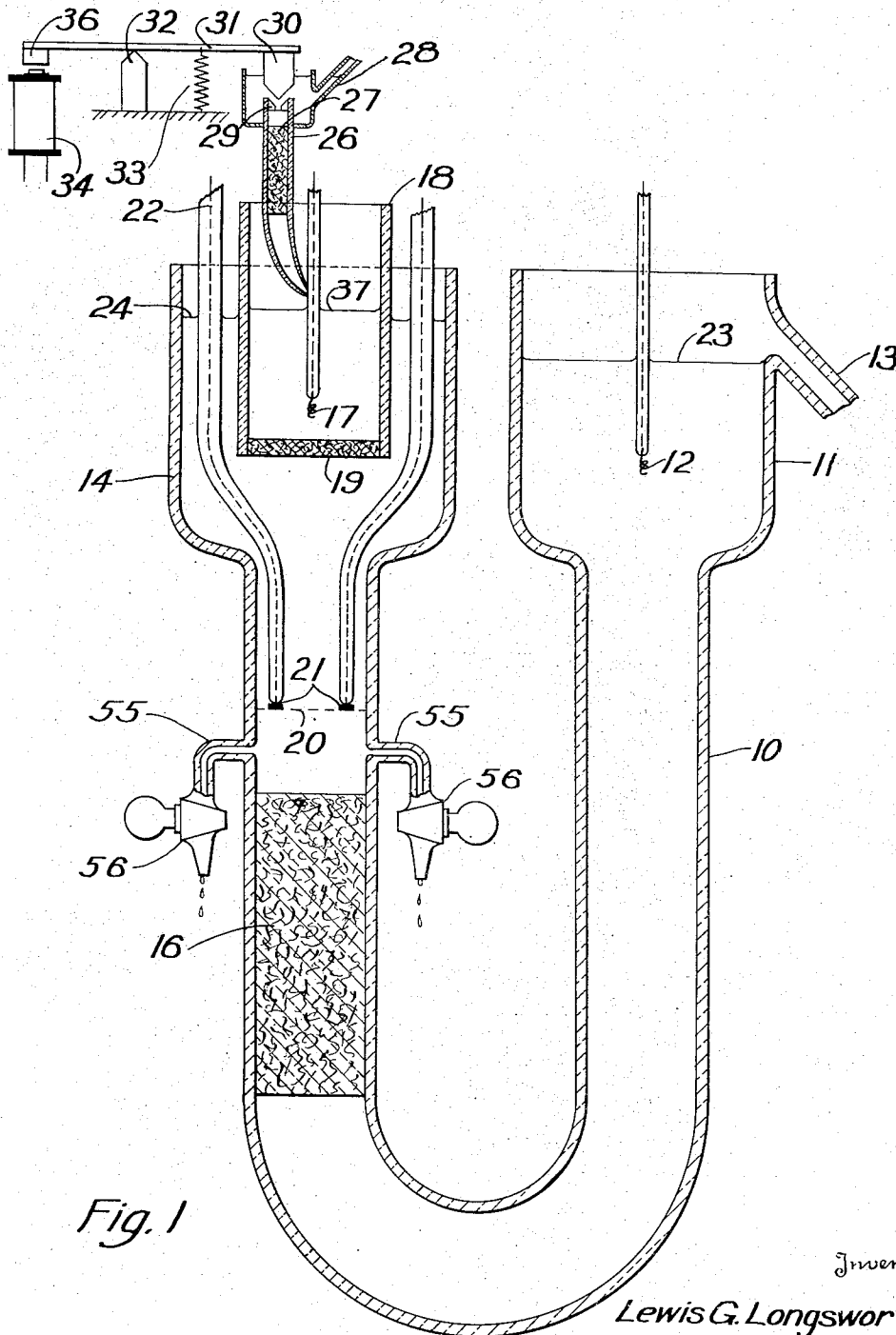
Aug. 7, 1951

L. G. LONGSWORTH
METHOD AND APPARATUS FOR CONTROL OF BOUNDARY
BETWEEN ELECTROLYTIC FLUIDS

2,563,729

Filed Feb. 3, 1945

2 Sheets-Sheet 1



Inventor

Lewis G. Longworth

By Robert A. Lawrence

Attorney

Aug. 7, 1951

L. G. LONGSWORTH
METHOD AND APPARATUS FOR CONTROL OF BOUNDARY
BETWEEN ELECTROLYTIC FLUIDS

2,563,729

Filed Feb. 3, 1945

2 Sheets-Sheet 2

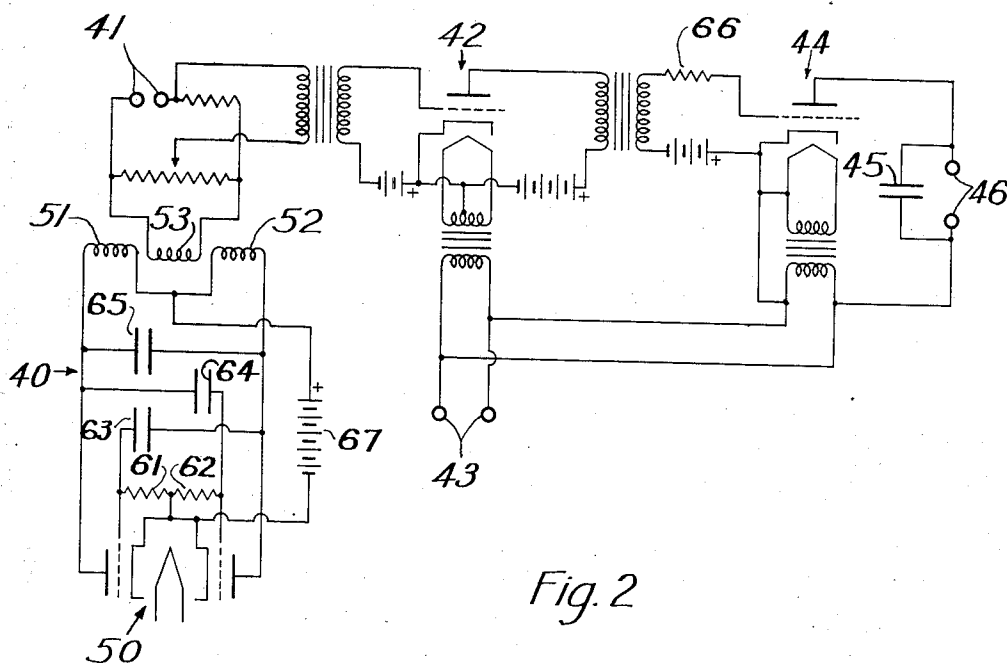


Fig. 2

Inventor

Lewis G. Longworth

By *Robert A. Savender*
Attorney

UNITED STATES PATENT OFFICE

2,563,729

METHOD AND APPARATUS FOR CONTROL
OF BOUNDARY BETWEEN ELECTROLYTIC
FLUIDS

Lewis G. Longworth, New York, N. Y., assignor
to the United States of America as represented
by the United States Atomic Energy Commis-
sion

Application February 3, 1945, Serial No. 576,122

7 Claims. (Cl. 204—1)

1

My invention relates to apparatus for main-
taining a boundary between fluids of different
conductivity and, more particularly, to a device
in which one fluid is superposed on another and
the circumstances are such that the location of
the boundary between them may be maintained
or shifted by the addition of quantities of one
of the fluids.

For examples, in systems for the electrolytic
separation of isotopes of a metal it has been
found that the addition of an acid at the cath-
ode will cause a counterflow which may be con-
trolled to sweep back ions of a heavy isotope and
permit the collection at the cathode of the more
mobile ions of a lighter isotope. It is known
that in such a system the rate of counterflow
must be carefully regulated, since an insufficient
counterflow will permit the less mobile ions to
reach the cathode while excessive counterflow
will sweep back ions of both heavy and light
isotopes. In other words the rate of counter-
flow must be such that the ions of the heavy iso-
tope will be swept back and the more mobile ions
permitted to pass to the region of the cathode.

I have discovered that the rate of counterflow
may successfully be controlled by measuring the
conductivity of the electrolyte at a given point
in the system, preferably at a location nearer the
cathode than the anode, and varying the rate
of acid addition proportionally with the conduc-
tivity of the electrolyte at the chosen spot. This,
in effect, establishes and maintains a boundary
between the electrolyte solution and the highly
acid solution disposed at the region of the cath-
ode.

One object of my invention is to provide means
for automatically regulating the position of the
boundary between fluids of differing conductivity,
in a system wherein one fluid is superposed on
another. Another object of my invention is to
control the rate of counterflow in an electrolytic
system for the separation of isotopes so that less
mobile ions are effectually retarded and more
mobile ions are permitted to reach the cathode
region. Parenthetically, it should be observed
that complete separation of the isotopes is not
obtained, the end result being a solution en-
riched as to the concentration of the lighter iso-
tope or isotopes.

Another object of the invention is to provide
an automatic, self-regulating control for the
counterflow in an electrolytic system for the sep-
aration of isotopes.

A further object of the invention is to sim-
plify and render commercially practical isotope

2

separation in an electrolytic system wherein a
counterflow is employed to sweep back less mo-
bile ions and permit the passage of more mobile
ions.

An important feature of my invention resides
in the combination of a pair of control elec-
trodes inserted in an electrolytic system in a
plane normal to the direction of the electrolyz-
ing current, a bridge circuit so connected that the
fluid between the control electrodes forms a part
thereof, and means responsive to the conductivity
of the fluid at these electrodes for controlling
the addition of a fluid to the electrolytic system.

Another feature of the invention resides in a
novel electrical control wherein high frequency
alternating current is passed through a bridge
circuit in which one leg comprises a portion of an
electrolyte and in which a thyatron relay is ar-
ranged to operate a magnetic burette when the
conductivity of the electrolyte varies by a prede-
termined amount.

Among the advantages which result from the
practice of my invention is the fact that the
automatic control of the counterflow makes it
possible for a single attendant to supervise the
operation of a large number of separators. The
expense of operation is still further reduced in
view of the fact that the automatic control fea-
ture renders the system more efficient than sep-
arators in which the counterflow is regulated by
an attendant who can only estimate the extent
to which additional fluid must be added to the
system from time to time.

These and other objects and features of the
invention will more readily be understood and ap-
preciated from the following detailed description
of one embodiment thereof selected for purposes
of illustration and shown in the accompanying
drawings in which:

Fig. 1 is a diagrammatic view, partly in cross-
section, of an electrolytic system for the separa-
tion of isotopes in which my invention has par-
ticular application, and

Fig. 2 is a schematic circuit diagram of ap-
paratus employed in practicing the invention.

As shown in Figure 1, an apparatus for the sep-
aration of isotopes of a substance may include a
U-shaped glass tube 10, provided at one end with
an enlarged cup-shaped portion 11 into which an
anode 12 is inserted. A spillway 13 is formed in
the wall of the tube at the anode region 11. Similarly, the other end of the U-shaped tube 10
is enlarged to provide a cup-shaped cathode re-
gion 14 into which a cathode 17 is inserted. Dis-
posed in the tube 10 in the leg of the U beneath

the cathode 17 is a plug 16 of sintered glass. A glass cup 18 surrounds the cathode 17 and has for its bottom wall a sintered glass diaphragm 19. The anode 12 and the cathode 17 are the working electrodes.

It will be understood that the apparatus may be used for the separation of isotopes of any metal of which the ionized isotopes possess different mobilities. By way of example, potassium has isotopes K^{39} and K^{41} , the ion of K^{39} being more mobile in an electrolyte than the ion of K^{41} . In carrying out the separation, a solution of KCl may be poured into the glass tube 10 at the anode end, while HCl solution is periodically added at the cathode as will be more fully explained below. When a potential is applied to the anode and cathode electrodes, 12 and 17, chlorine ions will be drawn to the anode 12 and potassium ions of both isotopes will move toward the cathode 17. The function of the sintered glass plug 16 is to minimize remixing by turbulence and convection. The plug permits the flow of ions but also quiets the flow through the separating zone. The lighter K^{39} ions, of higher mobility, will tend to accumulate around the cathode at a faster rate and the less mobile isotope ions, i. e. those of the heavier K^{41} , but if no further steps are taken and time is allowed to elapse, both isotopes will eventually gather at the cathode 17. However, by adding liquid at the cathode while maintaining a sufficient number of ions (other than K ions) in such liquid to insure the desired electrolytic flow of current between the working electrodes, the resulting hydrodynamic flow of liquid toward the anode will oppose the electrolytic migration of potassium ions toward the cathode, and if the rate of flow of the added electrolyte is appropriately balanced against the K ion migration, the K ions can be, in effect, selectively retarded in an inverse relation to their mobilities.

Thus in the system shown, by the addition of HCl (i. e. an aqueous solution of hydrochloric acid) at the cathode region at a carefully determined rate, the heavy K^{41} ions will tend to be swept back more than the lighter and more mobile K^{39} ions, or rather, the latter will be more able to overcome the counter flow and will progress further toward the cathode 17. Under presently preferred conditions, the flow is adjusted so that few, if any, of the potassium ions actually reach the cathode, and a so-called boundary between HCl and KCl solutions is thus formed (provided the HCl is added to the solution at the proper rate), advantageously at a point in the system between the cathode and the plug 16, e. g. as indicated by the reference character 20. Under proper conditions the boundary can actually be seen, because of difference of index of refraction of the two solutions. The K^{39} ions tend to migrate to the region of this boundary, while the counter-flow retards the K^{41} ions to a greater extent, so that a gradient of the relative concentration of K^{39} to K^{41} ions can be established between the boundary and the anode region. But for continued addition of HCl at the cathode region, the boundary would move toward the cathode, and consequently a boundary of this general type has sometimes been called a "moving boundary"; in carrying out the present invention, the boundary is preferably restrained from so moving, by automatically adjusted feed of electrolyte, i. e. HCl, into the system at the cathode region. It will now be seen that as the system continues to operate, a separation or enrichment of the isotope K^{39} is established and maintained in the zone at

and just below the boundary, and by appropriate means, enriched solution can be withdrawn from this zone. The remainder of the apparatus to be described functions to maintain the boundary between the solution of KCl and HCl.

A pair of platinum electrodes 21, i. e. the control electrodes, having their connecting wires encased in glass tubes 22, are inserted from the cathode end of the tube 14 and disposed in the plane of the desired boundary 20. A burette 26 is disposed with its lower open end within the glass cup 18 at the region of the cathode 17. A plug 27 of sintered glass is disposed in the burette adjacent its lower end, and an inlet tube 28 may communicate with a larger reservoir or container of HCl (not shown). In the lower part of an upper, enlarged portion of the burette 26, and below the inlet 28, is a valve comprising a rubber plug 29 driven into the burette and providing a valve seat with which a closure member 30 is arranged to cooperate.

The closure 30 is carried on the end of an arm 31 mounted for pivotal movement on a pivot 32 and is normally held in contact with the valve seat by means of a tension spring 33. The other end of the arm 31 carries an armature 36 cooperating with a solenoid 34 which is adapted to be operated in accordance with the tendency of the boundary 20 to shift, as will hereafter be explained.

The circuit shown in Fig. 2 comprises a multivibrator 40 including a twin triode tube 50 of a type well known in the art such as a 6N7. The high frequency multivibrator itself, which may be in the form of a so-called push-pull negative resistance oscillator, forms no part of my invention and, as shown is composed of elements connected in a manner well known in the art. The electrodes 21 are connected to terminals 41 (Fig. 2), and it will be seen that the electrodes 21 and the fluid between them form one leg of a Wheatstone bridge circuit. The output of the multivibrator 40 is applied across the bridge circuit through two primary windings 51 and 52 and a secondary coil 53 (included as the input of the bridge circuit). The output of the bridge circuit is transformer coupled to a triode amplifier tube 42, the circuits of which are arranged in a manner well known to the art. A 6F5 tube may be conveniently used in the amplifier. A. C. power is applied to the circuit at the terminals 43. The output of the amplifier 42 is applied to a conventional thyatron relay circuit 44. Again, the details of the thyatron relay form no part of my invention, and the relay circuit is constructed and arranged in a manner well known in the art. An FG 57 tube may conveniently be used in the thyatron circuit. The solenoid 34 is included in the plate circuit of the relay 44, the connections being made to the terminals 46. It is evident that the circuit may be adjusted so that the Wheatstone bridge is balanced to deliver a voltage insufficient to fire the thyatron relay 44, this condition being obtained when the electrodes 21 are disposed in a relatively concentrated solution of HCl.

When the electrolytic process takes place in the system, the ions of the isotopes of potassium will drift toward the cathode 17 and the conductivity of the solution lying between the electrodes 21 will decrease; that is, the boundary will move up, toward the cathode 17. When this happens, the bridge circuit is thrown out of balance, and a pulse will be delivered to the amplifier 42 where it will be amplified and delivered to the relay 44

as a voltage sufficient to fire the thyatron. The operation of the thyatron will energize the windings of the solenoid 34, draw down the armature 36 on the arm 31, and open the valve 30. This permits HCl to flow from the burette into the cup 18, the level of HCl in the cup being indicated by the reference character 37. HCl will continue to be added to the system until the boundary between the HCl solution and the KCl solution is shifted back to the plane 20. The conductivity of the solution between the electrodes 21 will then be restored to its initial value, the bridge circuit will then be balanced, and the solenoid 34 will be de-energized thus permitting the valve 30 to close and shut off the flow of HCl through the burette. A condenser 45, adapted to have a filtering or smoothing effect, is shunted across the terminals 46 in the plate circuit of the thyatron in accordance with principles well known in the art, and improves the operation of the solenoid 34. I have found that 20 mfd. is approximately the proper value for the condenser 45.

Although, the apparatus of my invention functions in a step-by-step manner, the result is a flow of HCl from the cathode region at a rate sufficient to keep the boundary essentially stationary and thus to retard preferentially the less mobile K^{41} ions while permitting the passage of the more mobile K^{39} ions into the region of the boundary. Means may be provided for withdrawing from the boundary region solution which is rich in K^{39} as compared to K^{41} , for example, one or more tubes 55, conveniently of capillary or near-capillary internal diameter, mounted to extend into the liquid below the boundary 20 and provided with stopcocks 56. Whether the withdrawal is continuous or intermittent through means of the sort shown, or whether the operation is simply stopped from time to time to permit introduction of other devices for removing enriched solution, care should be taken to avoid agitation or mixing with unwanted portions of liquid. KOH may be added at the anode from time to time to replenish the supply of potassium ions.

Although lower frequencies may be used in some cases, it seems preferable that the oscillator 40 supply a relatively high frequency to the bridge circuit of Fig. 2, say of the order of 1000 cycles per second or even considerably higher, to facilitate prompt and efficient response of the thyatron 44 and the solenoid 34 in the circuit shown, and to minimize electrolytic disturbance between the electrodes 21. Purely by way of example, and with the understanding that other values may be used, or other circuit arrangements, the following are particulars of one satisfactory circuit of the type of Fig. 2 that was used with the tubes mentioned above: Resistors 61 and 62 were 10,000 ohms apiece, condensers 63 and 64 each 0.1 mfd. and condenser 65 was 0.02 mfd. The independent inductance of each of coils 51 and 52 was 30 millihenries, and that of coil 53 was 60 millihenries, the latter being coupled to the former. The tube 42 was operated with a plate supply of 90 volts and a negative grid bias of 3 volts, and the negative grid bias of the thyatron stage 44 was 6 volts, supplied through a limiting resistor 66 of 0.1 megohm. Terminals 43 were connected to 110 volts A. C., and the oscillator plate battery 67 was 45 volts.

Since it is preferable to avoid having the control electrodes pick up an IR drop due to the electrolyzing current between the working electrodes, the control electrodes 21 in the apparatus

shown lie in a plane normal to the direction of the electrolyzing current, i. e. are disposed at least approximately on an equipotential surface in the fluid. It will also now be appreciated by those familiar with conductivity measurements, that the electric current passed through the fluid between the control electrodes 21 (as distinguished from the electrolyzing current between the working electrodes 12 and 17) is preferably kept to a minimum consistent with desired sensitivity and reliability of response.

It will be understood that the apparatus of my invention may be used to effect the separation of isotopes of any metal wherein the isotopes are sufficiently different in mass to permit their segregation by a counterflow as disclosed herein. Furthermore, it will be obvious to those skilled in the art that other electrolytes may be used in the separation of potassium isotopes. For example, KNO_3 and HNO_3 may be used instead of KCl and HCl. With different metals and different solutions, the rate of counterflow will differ.

In its broad aspects, my invention contemplates controlling the boundary between juxtaposed solutions in an electrolytic system by measuring the conductivity of the fluid at a point in the system and using that measurement to control the rate at which one of the solutions is added to the system. Accordingly, it is to be understood that other types of circuits could be employed for the same purpose and that the particular circuit shown in detail herein is but one example of many different ways in which the invention may be applied.

I claim:

1. The method of establishing and maintaining an ionic boundary in a liquid medium containing dissolved ions while passing an electric current between electrodes immersed in the medium comprising the steps of establishing a counterflow of liquid to retard migration of said ions toward one of said electrodes inversely in accordance with the mobilities of said ions by supplying an electrolyte substantially free of such ions in the path of the ions toward said electrode, and thereby establishing a boundary between said electrolyte and liquid containing the aforesaid ions that tends to move toward said electrode, detecting change in electrical characteristics of said liquid at a point where it is desired to maintain said boundary, said change being representative of movement of said boundary, and converting the detected change in electrical characteristics of liquid into modification in the aforesaid supply of electrolyte in a direction to counteract the last mentioned movement of the boundary.

2. A method of controlling distribution of ions in a liquid stream which comprises subjecting said ions to the electrolyzing action of charged electrodes in said stream, measuring the conductivity of said stream at a point between said electrodes and controlling the rate of flow of said stream in relation to the conductivity of said stream at said point.

3. A method of positioning an ionic boundary in a liquid stream which comprises subjecting said ions to the electrolyzing actions of charged electrodes in said stream, measuring the electrical conductivity at the desired boundary position and controlling the rate of flow of said stream countercurrent to the motion of said boundary toward one of said charged electrodes in response to changes in conductivity of said stream at the desired boundary position.

4. A method of positioning an ionic boundary

in a liquid stream which comprises flowing said stream between two charged electrodes to cause ions in said stream to tend to move in a direction countercurrent to said direction of flow, measuring the electrical conductivity in said stream at a point at which it is desired to maintain said boundary, flowing a liquid which is free from said charged ions past one of said electrodes so as to sweep back the ions attracted toward this electrode and controlling the rate of flow of said liquid responsive to changes in conductivity at the desired boundary point caused by the shift of said ions toward and away from said charged electrode.

5. In electrolytic apparatus comprising two electrolyzing electrodes positioned in a vessel and each immersed in a solution of different electrical conductivity, means for maintaining the ionic boundary between said solutions which comprises conductivity detecting electrodes positioned at the desired boundary transversely to the direction of current flow between said electrolyzing electrodes, a valve at one of said electrolyzing electrodes for admitting one of said solutions to said vessel, a supply container with which said valve communicates, a source of electric potential operably connected across said conductivity detecting electrodes and an electric circuit acting in response to changes in resistance between the said conductivity detecting electrodes to operate said valve and thereby to control the flow of solution from said supply container.

6. In electrolytic apparatus comprising two electrolyzing electrodes positioned in a vessel with each immersed in a solution of different electrical conductivity, means for maintaining the ionic boundary between said solutions comprising a pair of conductivity detecting electrodes disposed at the desired boundary normal to the direction of current flow between said electrolyzing electrodes, a solenoid-operated burette at one of said electrolyzing electrodes for containing and admitting one of said solutions to said vessel, a source of electric potential operably connected across said conductivity detecting electrodes and an electric circuit acting in response to changes

in resistance between the said conductivity detecting electrodes to operate said burette and thereby to control the flow of said solution from the burette.

7. In electrolytic apparatus comprising a generally U-shaped vessel having an electrolyzing electrode in each arm of said vessel with each electrode immersed in a solution of different electrical conductivity, means for maintaining the ionic boundary between said solutions which comprises conductivity detecting electrodes positioned in one arm of said vessel relatively close to the electrolyzing electrode therein and normal to the direction of current flow between said electrolyzing electrodes, a burette at the last said electrolyzing electrode for delivering solution to said vessel, a source of electric potential operably connected to said conductivity detecting electrodes and an electric circuit acting responsively to changes in resistance between said conductivity detecting electrodes to operate said burette and thereby to control the flow of solution from said supply container.

LEWIS G. LONGSWORTH.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,145,509	Pike et al.	July 6, 1915
1,388,613	Simsohn	Aug. 23, 1921
2,004,569	Davis	June 11, 1935

FOREIGN PATENTS

Number	Country	Date
88,280	Switzerland	July 1, 1921
302,490	Great Britain	Dec. 20, 1928

OTHER REFERENCES

Proceedings of the National Academy of Sciences, volume 9, (1923), pages 75 through 78.

Creighton and Koehler, Electrochemistry, 4th edition, volume 1, published 1944 by John Wiley & Sons, Inc., London, pages 129, 139 and 140.