

Nov. 13, 1962

G. DE VARDA  
MULTICELL ELECTROLYTIC FURNACE, INCLUDING  
APPARATUS FOR RAPID STARTING THEREOF

3,063,931

Original Filed Jan. 28, 1958

3 Sheets-Sheet 1

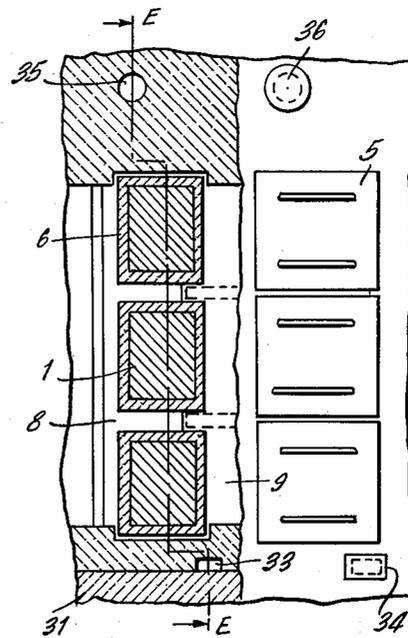
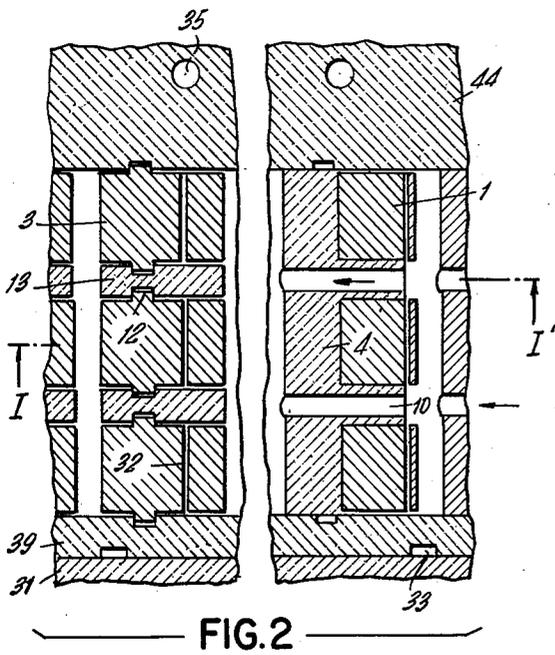
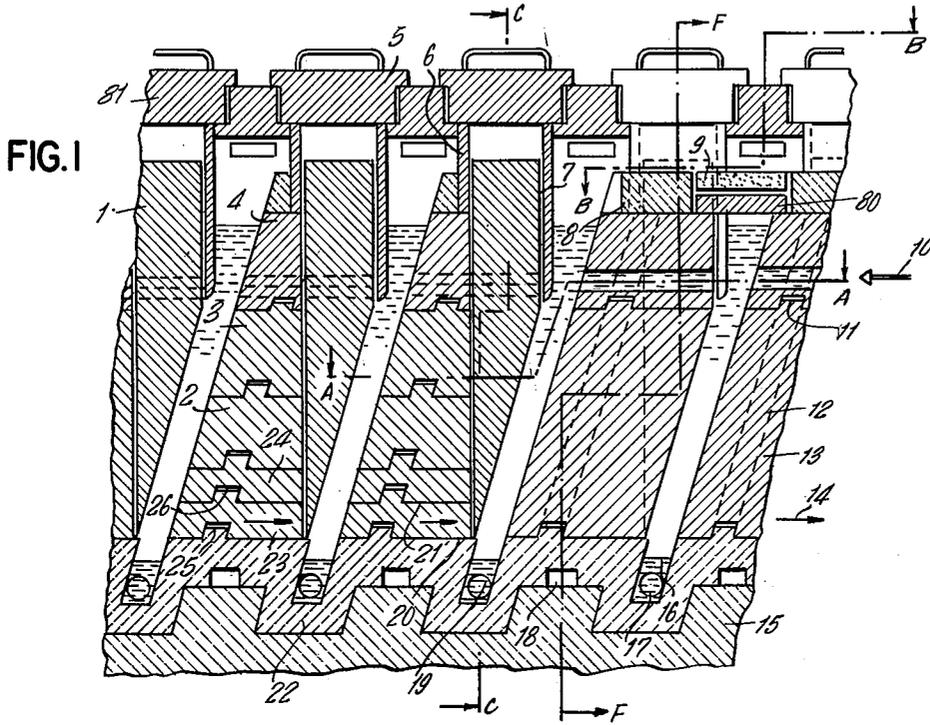


FIG. 3

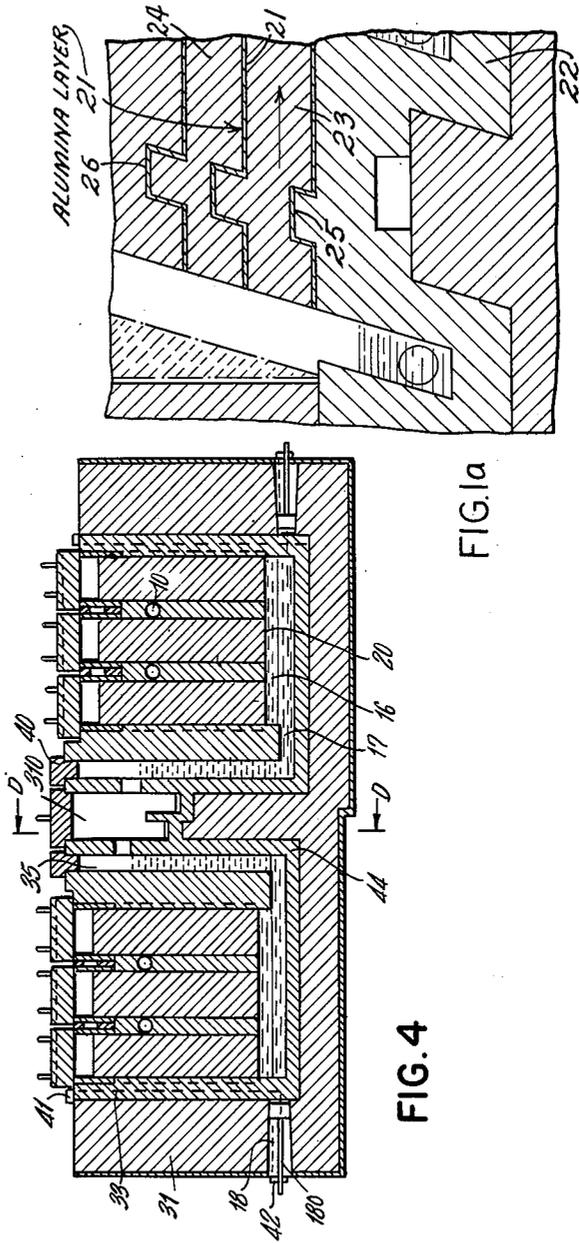
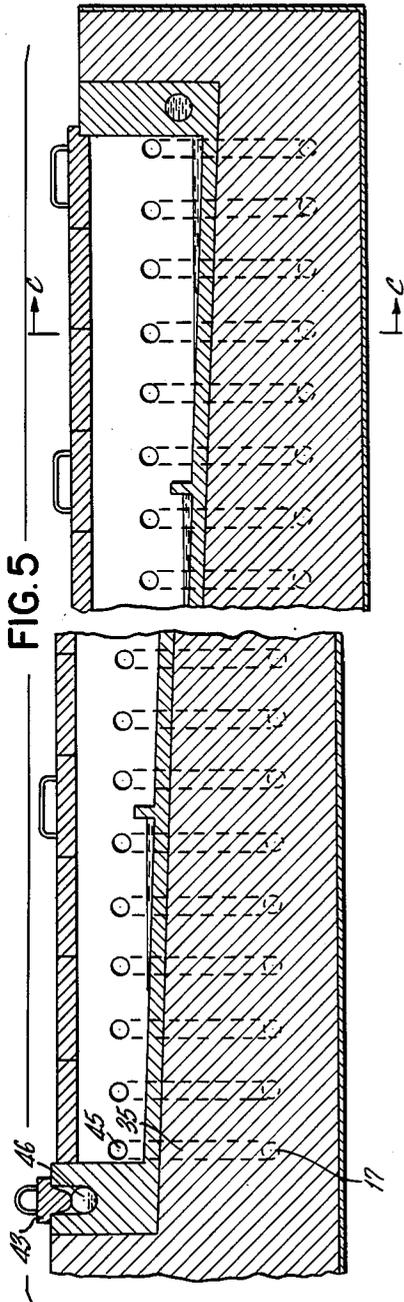
Nov. 13, 1962

G. DE VARDA  
MULTICELL ELECTROLYTIC FURNACE, INCLUDING  
APPARATUS FOR RAPID STARTING THEREOF

3,063,931

Original Filed Jan. 28, 1958

3 Sheets-Sheet 2



Nov. 13, 1962

G. DE VARDA  
MULTICELL ELECTROLYTIC FURNACE, INCLUDING  
APPARATUS FOR RAPID STARTING THEREOF

3,063,931

Original Filed Jan. 28, 1958

3 Sheets-Sheet 3

FIG. 7

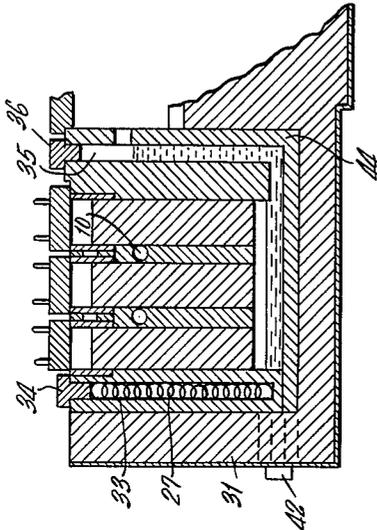
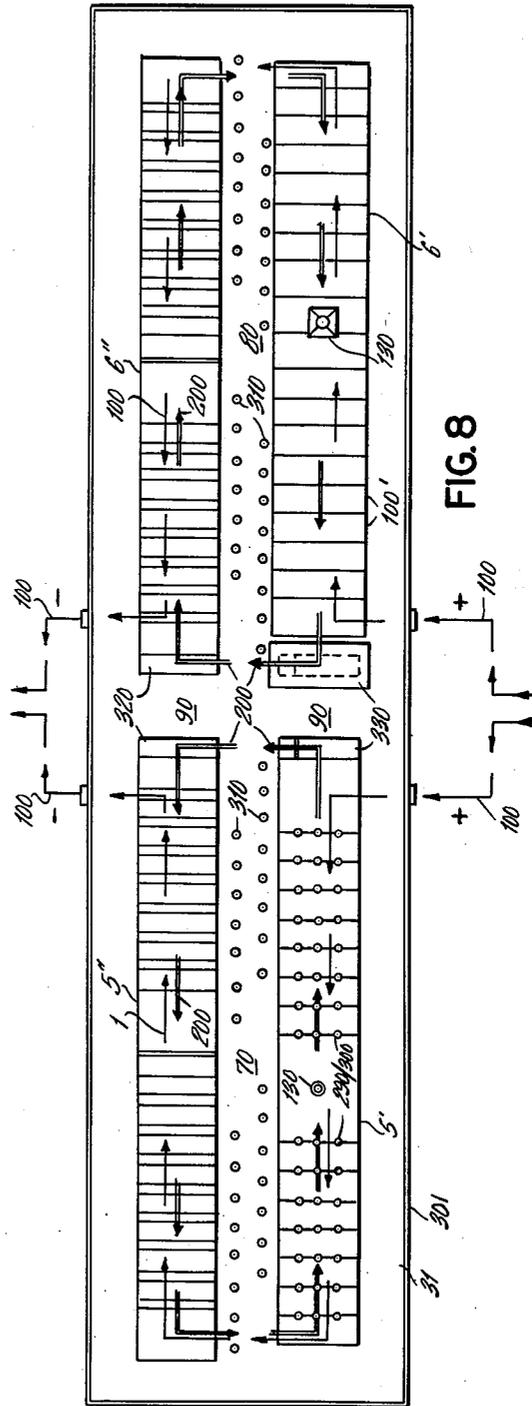
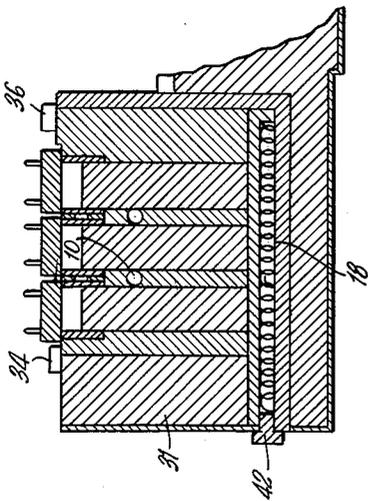


FIG. 6



1

3,063,931

## MULTICELL ELECTROLYTIC FURNACE, INCLUDING APPARATUS FOR RAPID STARTING THEREOF

Giuseppe de Varda, 8 Via San Sisto, Milan, Italy

Original application Jan. 28, 1958, Ser. No. 711,660. Divided and this application Oct. 29, 1959, Ser. No. 847,538

Claims priority, application Italy Jan. 31, 1957  
3 Claims. (Cl. 204-244)

This application is a division of my application Serial No. 711,660, filed January 28, 1958, U.S. 2,959,528, which is directed to the process. The disclosures are in all important aspects alike or similar.

This invention relates to an apparatus for the comparatively quick starting of multicell electrolytic furnaces, particularly those employing fused salt baths contained in inclined or vertical individual cells. It especially relates to the starting of a battery, or closed neckless chain or circuit, of closed electrolytic cells employed to produce aluminum by electrolysis of alumina at temperatures, for example, of from 900° to 1000° C., in a fused fluorinated salt bath, such as cryolite.

The principal object of this invention is to provide an apparatus for facilitating the rapid starting of multicell, or "necklace," furnaces of the types described in the G. de Varda applications Serial No. 587,985, filed May 29, 1956, U.S. Patent 2,952,592, Serial No. 711,577, filed January 28, 1958, and Serial No. 706,077, filed December 30, 1957, U.S. Patent 2,959,527. The starting of such multicell, or "necklace"-type electrolytic furnaces, equipped with anodic restoring layers, and with devices for continuously removing the aluminum produced, is possible by adapting known methods. For example, it is possible to introduce, while the furnace is empty, transportable resistors into the individual interelectrode gaps, as well as into the upper terminal chamber, lower terminal chamber, and alumina feed chamber etc. of the necklace-type furnace. Heating is effected by passing current through mobile resistors until the interior of the furnace has attained the desired temperature, for example 900° to 950° C., whereafter the resistors are removed. Fused bath is then fed into all the cells and the anodic restoring layers are set in place, if needed. The electrolysis process is then at once started by applying voltage to the terminals of the furnace. A method of this type, however, presents inconveniences, since the electrolysis process cannot be started until all the cells of the necklace-type circuit have been made ready. These cells may be quite numerous, thirty for example. Making them ready requires time, so that the fluid bath first fed into the cells may tend to solidify. This interrupts the passage of current through the furnace and eventually blocks all the furnace cells. In such case it is hardly possible either to heat the cells to complete bath fluidification, or to discharge their contents. The only thing that remains to be done is to scrap the cells when the solidification of the bath is terminated.

The danger of blocking is also present when it is necessary to start a "necklace-type" furnace which is equipped with continuously self-restoring electrodes, and with overflow devices for continuously removing the aluminum from the cells as soon as it is produced.

The said inconveniences, and also others, are eliminated by adopting the apparatus and starting procedure hereinafter described.

An illustrative example of a preferred convenient embodiment of the present invention is constituted by and explained with respect to the accompanying drawings, in which:

FIG. 1 is a longitudinal section taken at the two planes I—I' of FIG. 2, of a number of adjacent cells of a closed

2

bath circuit, electrolysis furnace for aluminum production, with provision for continuous tapping of aluminum, and having fixed and stationary electrodic blocks provided with juxtaposed self-restoring layered anodes, said blocks modified in accordance with the present invention; said section at vertical planes I—I' is taken across the right structure of FIG. 2 on plane I, and then on another plane I' in the left structure;

FIG. 1A is a fragment of FIG. 1, illustrating alumina coatings between anode layers;

FIG. 2 is a composite horizontal sectional view taken at different intermediate levels, at A—A of FIG. 1;

FIG. 3 comprises in part a top view and in part a horizontal section, being taken at B—B of FIG. 1;

FIG. 4 is a vertical transverse section, at C—C of FIG. 1;

FIG. 5 is a vertical section, at D—D of FIG. 4, taken parallel and close to its longitudinal axis;

FIG. 6 is a vertical section at line F—F of FIG. 1;

FIG. 7 is a vertical section at line E—E of FIG. 3;

FIG. 8 illustrates the connection of the cells in a necklace, being substantially as described in my prior application Serial No. 587,985, filed May 29, 1956.

The liquid levels indicated in the five figures are those attained at the termination of the furnace starting operation.

The internal cavities or surfaces of the furnace in contact with the bath are, as is known, protected by a refractory lining, for instance of magnesium oxide. The latter may be treated for instance as described in my application Serial No. 705,374, filed December 26, 1957, U.S. 2,952,605, to make them practically impermeable by the bath, maintaining however an electric resistivity higher than that of the fused bath, and, or, by other methods.

Reference may be made to the above-mentioned pending applications for more complete descriptions of the furnace elements and of the assembled furnace.

In FIG. 1 is shown a number of upwardly-downwardly extending, inclined bipolar electrodic structures. In the normal operation of the furnace, electrolysis current is introduced through a left end terminal electrode (not shown) constituting an anode electrodic structure. The current thence passes serially through the intermediate bipolar electrodic structures as indicated by arrow 14 of FIG. 1, and serially through the respective upwardly-downwardly extending intermediate electrolysis gaps, to a right end terminal electrode (not shown) constituting a fixed and stationary cathode electrode. The arrow at 10, in FIG. 1, indicates the counter-flow of the bath through the conduits 10 passing through the magnesia blocks 4 described below. These features are shown in my prior application Serial No. 587,985, U.S. 2,952,592. The upwardly-facing inclined surfaces of the stationary part of the bipolar electrodic structures provide, in the form shown in the drawing, the cathodically active electrode surfaces.

The stationary and fixed part of the bipolar electrode comprises a number of superposed, or stacked, carbon (preferably graphite) blocks or horizontal layers 2, 3, 23 and 24, surmounted by a magnesium oxide block 4, which in turn is surmounted by heat-insulating members 8. Bridging the top of each electrolysis gap is a supporting piece 80 of magnesium oxide, over which is placed the heat insulative cover plate 9. Refractory, chimney-shaped, conduit structures 6 extend through the outer heat-insulated wall 51. Conduits 6 are provided with removable cover 5.

As described in my application Serial No. 706,077, filed December 30, 1957, U.S. Patent 2,959,527, the anodic surfaces comprise, or are provided with, automatically

and continuously renewing anode surface elements or structure, which may comprise a single block 1 of prebaked carbonaceous electrode material, or an anodic assembly (not shown) of superposed blocks of the same material. The block 1 continuously descends, as the lower tip, resting upon the surface of ledge 20, is electrolytically consumed. The block is guided downwardly adjacent to the surface of the stationed parts 2, 3, 23, 24 by the chimney 6.

The bottom wall 15 (FIG. 1) and the lateral walls 31 (FIGS. 2, 3, 4) are each provided with an inner lining 22, 39 of magnesium oxide. Ledges 20 and ribs 25 are part of lining 22. Wall 15 and also lateral walls 31 are composed of or contain heat-insulating material. Any commonly employed heat-insulating porous refractory can be used. A horizontal groove 18 (FIG. 1) is formed in the lower face of each ledge 20, providing blind, horizontal channels 18. As shown in FIG. 4, the horizontal channels 18, which are normally provided with heat-insulating covers (not shown in FIG. 4), serve to permit introduction of mobile resistors 42. Blind vertical channels 33 (FIGS. 2, 3, 4 and 7) are formed between wall 31 and lining 39, into which vertical channels other mobile resistors 27 may be inserted. Each cell may be provided with at least one horizontal and one vertical blind channel. The resistors may be connected with one another. They are connected to a source of power and serve for heating the furnace in the various preparatory procedures, required, for example, for the various stages of impermeabilization with pitch (about 200° C.) and subsequent cooking (about 700° C.) and for the various starting stages (700° C. to 950° C.) of said furnace. The heat generated by the individual, mobile and transportable resistors, which are, for example of 3 kw. rating each, is transmitted through the refractory of magnesium oxide. The transmission is fairly good since its coefficient of heat conductivity is of the order of 0.006 cal/1 sec./1 cm.<sup>2</sup>/1° C.

The two graphite lower layers 23 and 24 of the bipolar electrode have reduced thickness, for example each one is 2 to 4 cm. thick, the upper layers 2 and 3 being, as indicated in FIG. 1, of greater thicknesses. The various layers 23, 24, 2 and 3 of the stationary part of the bipolar electrodes are placed into the individual cells. As shown in FIG. 2, the layers are provided with lateral projections to enable them to slide in the grooves 12. These grooves are formed in the sides of the inner walls 39 and 44 of the furnace, and also in the two small walls 13 (FIG. 2) which divide each bipolar electrode into three substantially equal portions. Wall 13 also divides the active electrodic surfaces into three cathodic zones and into three anodic zones.

Upon the upper face of each layer of electrodic graphite there is spread a veil or coating of alumina to reduce, to a minimum, electric contact with the overlying electrodic layer. For example (FIG. 1) face 21 of layer 23 is so coated before placing layer 24 on layer 23. FIG. 1A shows the coatings. The lower face of each layer has a recess 25, and the upper face has a corresponding projection 26, so the superimposed layers fit into each other. This is also the case with respect to the bottom non-conductive refractory ledge 20 and the upper refractory block 4, provided with recess 11. These indentations have, among other purposes, the function of securing good alignment of the layers of the graphite electrode, and also the required parallelism with the sliding plane 7 of the anodic restoring assembly 1 overlying the stationary part of the bipolar electrode.

In this way the easy and the perfect mechanical workability of graphite is utilized, by means of said indentations, to allow without inconveniences the not negligible thermal expansions and the contractions of the non-conductive refractory. The indentations maintain, to a significant extent, a barrier against the by-passage of bath

from one cell to the next. The passage should take place, at least prevailingly, through conduits 10 (FIG. 2) provided in non-conductive refractory blocks 4.

The ledges 20 under the electrodes, and also the side walls and the bottom 22 of the lower chambers serving to collect the metal, should be entirely impervious, with respect to the fused metal.

Finally, in the upper terminal chamber (not shown) at the head of the necklace of cells (see the reference to Serial No. 587,985 below), as well as in the lower terminal chamber (not shown) at the end of said circuit there are provided, at the top, electric resistors, preferably fixed, and also hatchways leading towards the outside to effect rapid control of liquid levels.

Electric resistors are also applied in the upper portion of the alumina feed chambers. These chambers, as well as the terminal chambers, are not shown in the drawings.

#### Furnace Starting Procedure

After its walls have been impermeabilized to the bath, which contains fused fluorinated compounds, such as cryolite, the furnace is completed by assembling therein, as already described, the stationary graphite parts of the bipolar electrodic structures, subdivided into various horizontal layers, and also the terminal electrodes (not shown) provided with metal conductors coming out preferably at the top of the furnace and connected by metal with the furnace terminals. Upper blocks of refractory 4, through which pass the channels 10, are placed thereto. The top insulation 8 and 9 for said blocks and for the opened bath surface is put in place, and also the chimney-shaped members 6.

Now the layers 1 constituting the restoring anodes are introduced into the empty and cold furnace and the correct position of the insulating pads 9 is made certain of, after which the covers 5 above the chimneys are carefully closed. The first stage of starting is now begun by feeding current to the flying or mobile resistors accommodated in the blind-bottom, horizontal channels 18 and the vertical channels 33, in the base and in the side walls respectively of the furnace, as well as the resistors (not shown) in the vertical tapping pockets 35 provided in the inner longitudinal dividing walls 44 of the furnace.

Upon heating gradually, the closed furnace is brought up to a temperature of about 700° C. It is convenient to provide an atmosphere of inert gas, for example by means of a stream of nitrogen, in order to avoid oxidation of parts 13, 22, 4, 39, 44.

At this time, the mobile resistors accommodated in the tapping pockets 35 are removed, and at once thereafter such a quantity of molten aluminum is poured into said pockets, that in the cell, and in the tapping pocket in communication therewith, it is above the level 20 (FIG. 1) of the MgO seat on which each stack of graphite bipolar electrodic layer confining the respective cells rests. However, although surpassing said level 20, it is convenient or best that the height of the metal should not be above the level 21 (FIG. 1) of the interstice between the lowest graphite layer and the immediately overlying one. In this way only the lower layer of each graphite stack is electrically connected with the adjacent ones in the necklace circuit, through metallic aluminum. Since the electrolysis is not yet begun, there is no need for the anode pieces 1 to be in place over said lower layers, at this stage.

This operation can be carried out in a limited time even if the number of cells is increased. Although the resistors have been previously removed from the tapping pockets in order to enable the introduction of fused aluminum, it is neither necessary nor convenient to cut off current from the transportable resistors remaining accommodated in the external walls. Having thus placed all the cells of the circuit in those conditions, one may now feed current to the furnace terminals.

The resistance of the path in the molten aluminum in each cell is negligible in practice. It is sensible however,

at the aluminum, graphite interfacial contact surfaces, and in the path through the individual base layers of the bipolar electrodes.

If now amperages equal to those of the full potentiality or capacity of the furnace in normal operation, corresponding for instance to 0.5 ampere for one square centimeter of active electrodic surface in a cell in normal operation, are made to pass through the furnace, the power absorbed will be, for example  $\frac{1}{10}$  of that of normal furnace operation.

At this time the passage to the second starting stage takes place, the furnace being kept closed, and while operating, for example, with a nitrogen atmosphere in the furnace. The maximum available or absorbable magnitude of direct current is made to pass through the bottom portions of the electrodes and the aluminum between them while the series resistors disposed in the external furnace walls are being energized at maximum. By proceeding in this way the inner furnace temperature increases gradually from 700 to about 900 to 950° C. Feeding of bath fluid to the high chamber (not shown) at the head of the necklace of cells, is then begun. A fluid bath rich in  $Al_2O_3$  is introduced into the closed circuit (FIG. 5) through the pocket at 43 and the channel 46 which constitutes the necessary connection between the two terminal chambers employed. Note Serial No. 587,985, filed May 29, 1956, U.S. 2,952,592, in this relation. The bath passes rapidly from the high chamber into the first contiguous cell, that is the one which, through conduit 17 (FIG. 5) is in communication with the pocket 35 provided with the overflow mouth 45, and from that one into the second one, and so forth, passing also through the alumina feed chambers to arrive at the last cell, the lowest one of the necklace. It then discharges into the low terminal chamber side with the high one.

This operation takes place in a comparatively limited time, for instance in one or two hours, without any need for disconnecting either the main furnace current or the one passing through the removable resistors.

As the fluid bath fills the electrolysis gap, of a given cell, the level 16 (FIG. 1) of the metal in the cell lowers, until the bath has completely displaced the metal from the interelectrodic gap. It is convenient, however, that the quantity of aluminum initially added should be such that when the cell fills with bath liquid the level of the metal in the cell should not descend below the level 19 so that bath liquid will not be introduced into the pocket 35 (FIG. 5) which should fill up with molten metal.

Consequently, the voltage drop in the individual cell increases until it reaches values sufficient to start the electrolytic process. The direct current amperage passing through the furnace as a whole tends to diminish, so that it may be convenient to adjust the current feeding the furnace to keep it constant.

The beginning of the electrolysis in all the cells of the circuit filled with bath liquid, marks the beginning of the third and last stage of the furnace starting operation. This stage comprises starting the device for lifting the bath from the low terminal chamber to the high terminal chamber. This can be done by means of an oscillating ladle as described in application on Serial No. 670,785, filed July 9, 1957, by G. Calabria, U.S. 2,991,240, or by means of a graphite pump as described in application Serial No. 705,373, filed December 26, 1957, of De Pava, as well as by other known devices.

Also the measuring devices for all of the alumina feeding stations must be started. It is necessary to thereafter adjust and check the delivery of the bath-lifting device. It is also necessary to check each cell with respect to the attaining of the temperature limits employed in normal operation. If provided, the conventional device for discharging the electrolytic gases from the upper chamber should conveniently now be put to operation. Finally, current may be shut off the circuit of the mobile resistors,

which when conveniently cooled, can be removed from the blind-bottom channels, and utilized, for instance, in subsequent operations for starting other furnaces. The channels should be preferably filled, for example with  $Al_2O_3$  powder, carefully closed and sealed with the plugs 41 and 42, after which the furnace may be considered completely started and by now put to normal productive operation. Channels 18 and 33 are termed blind channels because the molten liquids in the furnace have no access thereto. Obviously, the resistor 14 (FIG. 4) may be inserted farther into the channel 18.

In this description the term "order of magnitude" means differing by a factor of about one tenth. Thus, "order of magnitude" of 700° C. means the range of about 630° C. to 770° C.

The term "necklace of cells" signifies cells arranged to form a complete, closed circuit arranged for cyclic flow of bath liquid in the circuit, the electric current passing around the necklace serially through the cells, the bath liquid also passing serially, preferably in the opposite direction, while aluminum oxide is fed into the furnace at least at one point in the liquid circuit, and is carried to the cells by the cyclicly flowing bath liquid. Preferably the necklace is flattened, the cells being arranged at opposite sides of an internal wall longitudinally dividing the furnace. This arrangement, and the placing of the various tapping pockets, channels, feed chambers, etc. within the heat-insulating structure of the furnace, provides advantageous heat economy and facilitates the various operations.

FIG. 8 illustrates two necklaces of electrolysis cells, each of rectangular form with head ends joining each other, and having independent bath circuits electrically connected in parallel but accommodated within one single rectangular "twin" furnace. The single-line arrows 100 indicate the current path. The double-lined arrows 200 indicate the direction of the path of main circulation of the electrolysis bath. A lift device (not shown) lifts the bath from the lower level of chamber 330 to the upper level of chamber 320. A metal casing 301 contains a cell housing 31 formed of layers of refractory, comprising thermally and electrically insulating material, and also contains the four "branches" 5', 5'', 6', 6'', each branch constituting groups of cells. Each left and right pair of branches forms an independent necklace of cells, both being assembled into a twin furnace. The two longitudinal branches of each necklace have in common the longitudinal intermediate walls 70 and 80, and the two necklaces have in common a transverse intermediate wall 9. At the top of the cells insulation is provided by removable covers 100', corresponding generally to covers 5 of FIG. 1. Each longitudinal branch of the furnace is formed by a certain number of elementary cells of the type shown in FIG. 1. Alumina supply stations and devices are indicated at 130. At 290 are indicated vertical holes for insertion of plugs 300, which are employed to throttle the horizontal passages 10 shown in FIGS. 1 and 6. Aluminum tapping wells or pockets are indicated at 310.

I claim:

1. A multicell quick starting furnace for the electrolytic production of alumina from fused compounds, comprising a plurality of upwardly-downwardly extending bipolar electrode structures provided with upwardly-downwardly extending self-restoring anodic surface devices and having a stationary permanent and fixed part of the bipolar electrodes of graphite, characterized in that each graphite electrode is divided into at least two horizontal layers, the height of a lower layer being only a small fraction of the over-all height of the layers and that between said lower layer and the overlying electrodic layer a thin interstice is formed containing a layer of electrically non-conductive material to reduce to a minimum electric contact with the overlying electrodic layer.

2. A multicell quick starting furnace for the electro-

lytic production of alumina from fused compounds, comprising a plurality of upwardly-downwardly extending bipolar electrode structures provided with upwardly-downwardly extending downwardly feeding self-restoring anodic surface devices and having a stationary, permanent and fixed part of the bipolar electrodes of graphite, characterized in that each graphite electrode part is divided into at least two horizontal layers, the height of a lower layer being only a small fraction of the over-all height of the layers and in that said lower layer is separated from the overlying electrodic layer by a thin layer of substance which is not electric-conductive, to reduce to a minimum electrical contact with the overlying electrodic layer, the graphite layers being respectively provided with interdigitating projections and recesses, to maintain them in a predetermined form of alignment, to provide a flush surface, the self-restoring anodic surface device being located at said surface, said interdigitations constituting a hindrance to passage of bath liquid from cell to cell

through the interstices between the layers themselves and between the layers and the contacting refractory non-electric conductive elements.

3. The apparatus defined in claim 2, the thin layer comprising alumina and the thermal expansions and contractions of the refractory elements contacting the graphite electrodes being accommodated by the interdigitations.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

979,497	Hulin -----	Dec. 27, 1910
2,451,494	Johnson -----	Oct. 19, 1948
2,748,073	Mellgren -----	May 29, 1956

##### FOREIGN PATENTS

206,689	Australia -----	July 21, 1955
723,448	Germany -----	Aug. 5, 1942