

Feb. 9, 1926.

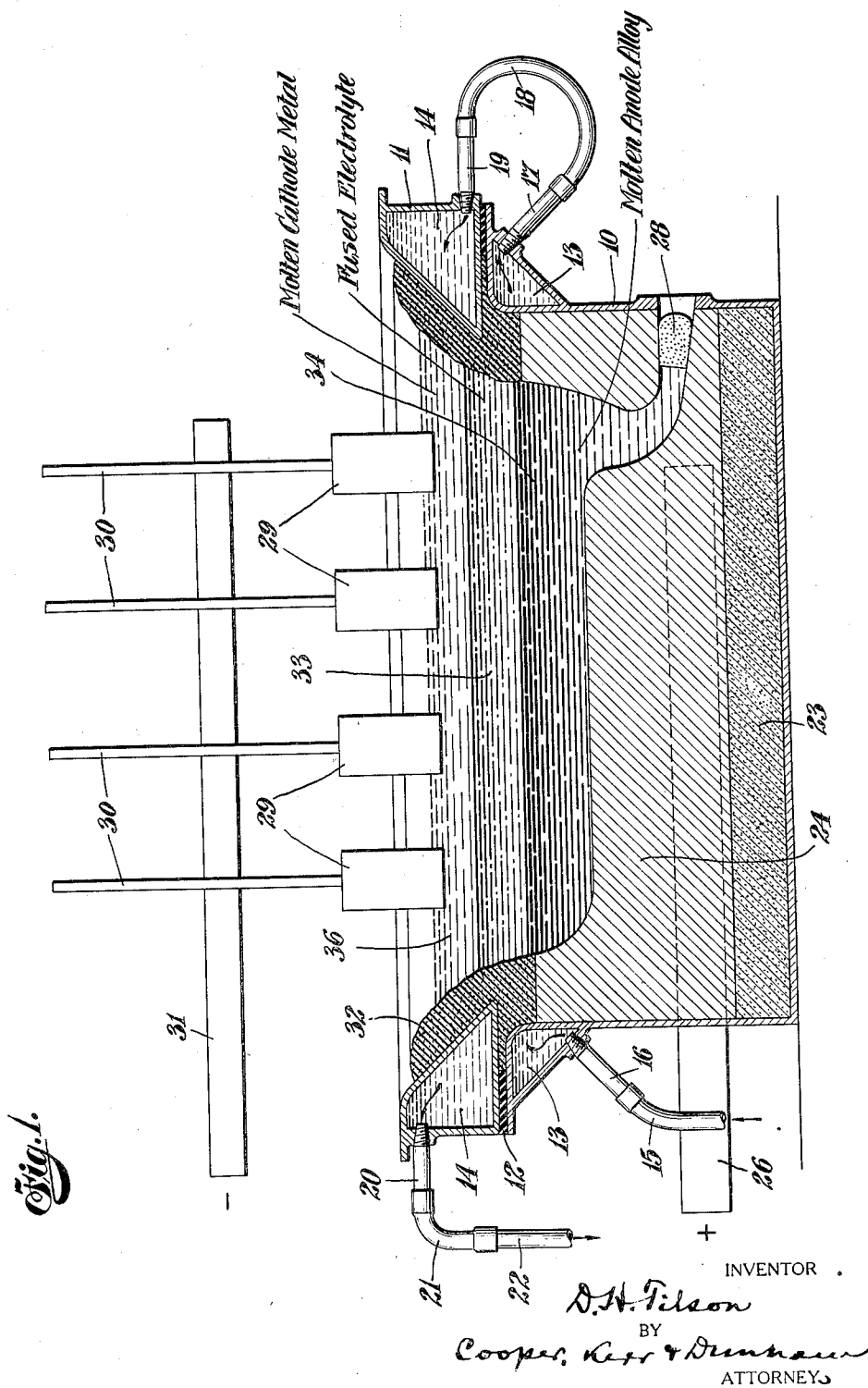
1,572,253

D. H. TILSON

METHOD OF STARTING ELECTROLYTIC CELLS

Filed Nov. 30, 1923

2 Sheets-Sheet 1



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Fig. 3.

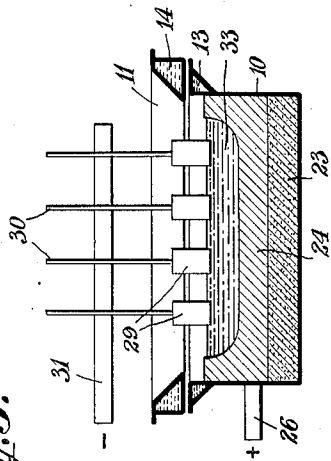


Fig. 5.

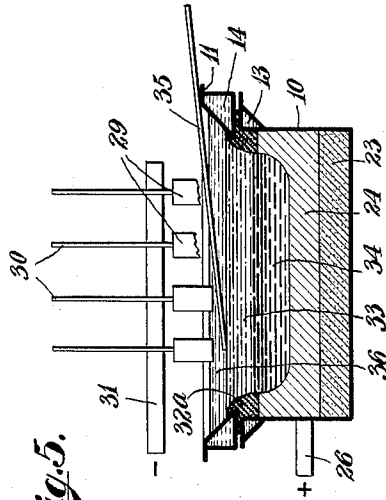


Fig. 2.

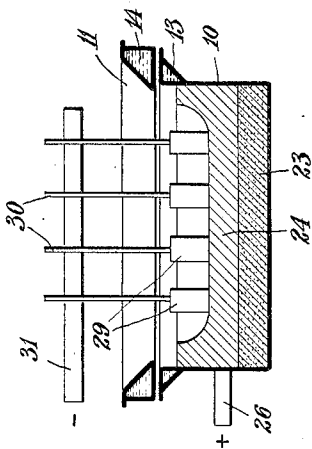
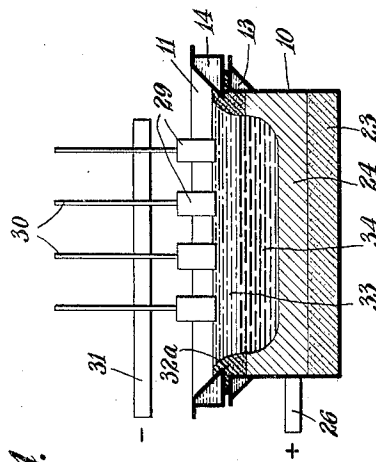


Fig. 4.



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UNITED STATES PATENT OFFICE.

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METHOD OF STARTING ELECTROLYTIC CELLS.

Application filed November 30, 1923. Serial No. 677,587.

To all whom it may concern:

Be it known that I, DONALD H. TILSON, a citizen of the United States of America, residing at Badin, in the county of Stanly and State of North Carolina, have invented certain new and useful Improvements in Methods of Starting Electrolytic Cells, of which the following is a full, clear, and exact description.

This invention relates to starting, or putting into condition for operation, electrolytic cells for the refining of metal, particularly cells of the type described in the copending application of William Hoopes, Serial No. 608,287 filed December 21, 1922, now Patent No. 1,534,320, issued April 21, 1925, in which the impure metal or alloy, the electrolyte or bath, and the refined metal deposited at the cathode, are in the molten state. The chief object of the invention is to provide for the purpose a method which can be performed in a short period of time, even under unfavorable conditions, with a minimum of labor, without excessive consumption of electric power, and without injury to the apparatus. To this and other ends the invention consists in the novel features hereinafter described.

A cell of the type referred to, as designed particularly for the electrolytic separation of aluminum in metallic form from an alloy thereof, is illustrated in the accompanying drawings, in which—

Fig. 1 is a cross section showing the cell in use, with the molten anode metal or alloy in the bottom of the cell, the fused electrolyte floating on the anode alloy, and the molten cathode metal floating on the electrolyte.

Figs. 2, 3, 4 and 5 are diagrammatic cross sections illustrating various stages in my present process.

The cell illustrated comprises a lower steel shell 10 of cylindrical form and an upper steel shell 11, the two constituting the lower and upper sections of the complete shell. The shell sections are secured together in any convenient manner, and are electrically separated or insulated from each other, as indicated by the insulating ring or gasket 12. They may be also provided with suitable cooling means, in the present instance water jackets 13, 14, in the neighborhood of the joint between the two sections. Cooling water is supplied to the lower jacket

through a pipe 15 and inlet nipple 16 and flows in both directions to an outlet pipe 17. Thence it passes through pipe 18 and inlet nipple 19 to the upper water jacket, in which it flows in both directions to the outlet nipple 20 and thence through pipe 21 to the waste pipe 22. To prevent electrical grounding, rubber hose may be used for the pipes 15 and 21 and rubber hose may be used for the pipe 18 to prevent material flow of current from the one cell section to the other. In the bottom is a layer of heat-insulating material 23, as for example powdered bauxite, and on this is a bottom lining 24 of conducting material, preferably carbon. Electrical connection, between the lower shell and the carbon lining therein, and the external circuit or source of current, not shown, may be made by means of a terminal or busbar 26 associated with the carbon lining in any convenient and suitable manner. The carbon bottom, which constitutes what may for convenience be termed the lower electrode of the cell, is formed with a cavity or depression in its top, as indicated, and with a tapping hole which may be closed by a plug 28 of suitable refractory material. The upper means for connecting the cell contents with the external circuit or source of current comprises a suitable number of short thick cylinders in the upper ends of which the copper or other metal rods 30 are secured. These rods are clamped or otherwise secured by suitable means, not shown, to the negative terminal or busbar 31. The cylinders 29 are preferably made of graphite, as described in the copending application of Francis C. Frary, Serial No. 672,867, filed November 5, 1923, now Patent No. 1,535,458, issued April 28, 1925.

On the sides of the cell is a thermally and electrically insulating lining 32 in close union with the carbon bottom 24 and extending over the joint between the shell sections to a plane well up in the upper section. My present process preferably includes the depositing of the side-lining or crust 32 on the sides of the cell, above but in close contact with the marginal portions of the carbon bottom lining. It may therefore be assumed that when the cell is ready for my present process it is substantially like that illustrated in Fig. 1, except for the presence of

the side crust or lining and the molten contents hereinafter described.

The first step of my process as carried out in the preferred way is to heat the carbon bottom lining. This is efficiently accomplished by lowering the graphite connectors or electrodes 29 into contact with the carbon bottom, as in Fig. 2 for example, and then connecting the cell terminals to the appropriate terminals of a suitable source (not shown) of direct current. Upon closing the circuit the flow of current through the high resistance encountered at the points of contact between the graphite connectors and the carbon bottom causes rapid and great evolution of heat at such points. When the carbon bottom lining has been well heated up, with considerable portions of it showing a dull red, I cut the cell out of the circuit and pour into the cell a suitable quantity of electrolyte or bath, which has in the meantime been melted in any suitable furnace, not shown. The nature of the electrolyte depends, of course, upon the use to which the cell is to be put. If aluminum is to be refined, the best electrolyte that I know of for the purpose is composed of a mixture of sodium and aluminum fluorids with the addition of barium or strontium fluorid or both, as for example in the proportions given in the copending application of William Hoopes, Francis C. Frary and Junius D. Edwards, Serial No. 608,285, filed December 21, 1922, now Patent No. 1,534,318, issued April 21, 1925. A fused bath compounded of the salts mentioned is of greater density than molten aluminum and is capable of dissolving a considerable quantity of alumina. In some cases it is desirable in the crust-forming stage of my process to have a substantial amount of alumina in the bath, say enough to saturate the same. It is to be understood, however, that the presence of alumina is not essential.

The cell is now connected to the circuit again and the connectors or electrodes 29 are raised, far enough to leave only their lower ends dipping into the molten bath, say to the extent of an inch or two. This stage is represented in Fig. 3, in which the molten bath is indicated at 33. Electrolysis now takes place, but has apparently no useful result except to maintain or increase the temperature of the molten bath. The electrical heating is, however, very important during the rest of the starting process, as it enables me to maintain the cell contents in the molten state at the working temperature at all times, and makes me independent not only of possible delays in obtaining anode alloy or cathode metal but also of variations in their preliminary temperatures. If adequate supplies of superheated molten bath, anode alloy and cathode aluminum are available, and the labor and me-

chanical conditions are such that the proper amounts of the materials named can be tapped into crucibles and brought to the cell at such a rate that the three substances can be deposited in rapid succession it is possible to start the cell without passing current through it (except, in some cases, for the preliminary heating of the carbon bottom) until all three layers are in place. However, if there is any delay, or if the anode alloy or the cathode metal becomes cooled below the freezing point of the electrolyte, portions of the latter may solidify at its upper or lower surface, as the case may be. Then when the current is applied, its concentration at the still fused areas of the electrolyte may be so great as to cause a swirling or boiling action (due to the magnetic fields present) which may be violent enough to cause the two metal layers to unite and thus require the operation to be stopped and the cell dug out and re-started.

Having established in the cell a layer of electrolyte carrying current as above described, I next introduce a suitable quantity of previously melted anode metal or alloy. For aluminum refining the anode metal must be heavier than the bath, so that it will sink through the bath to the bottom of the cell. Preferably the aluminum-containing anode metal is an alloy of aluminum, copper and silicon, low in iron and titanium, as described in the copending application of William Hoopes, Francis C. Frary and Junius D. Edwards, Serial No. 608,284, filed December 21, 1922. The anode alloy is supplied preferably through a trough (not shown) which delivers it to the center of the cell, pouring rather slowly so as to raise the bath layer gradually and avoid mixing the alloy therewith. Enough anode alloy is introduced to bring the upper surface of the bath layer well above the insulating joint between the two shell sections 10, 11, (say an inch or so above) as in Fig. 4, in which the anode alloy is indicated at 34; but not enough to bring the alloy itself into contact with the shell. As the bath mixture rises in contact with the shell the cooling effect of the water jackets 13, 14 causes a crust to freeze on the shell walls over the joint between the two sections. This crust, indicated at 32^a, Fig. 4, is substantially free from metal and has high insulating properties, electrically as well as thermally, and may attain a thickness of two inches or more. If the bath is saturated with or contains a substantial amount of alumina a considerable portion of the latter freezes out in crystalline corundum-like form (as described in the copending application of William Hoopes, Junius D. Edwards and Basil T. Horsfield, Serial No. 608,289, filed December 21, 1922, now Patent No. 1,534,322, issued April 21, 1925), making the side crust more refractory

and giving it better insulating properties, and at the same time diminishing the alumina content of the fluid electrolyte well below the saturation point.

5 The anode alloy is preferably supplied to the cell in molten form, but it may be in solid form. In the latter case, however, it must be melted by electrical heat, which entails considerably longer time for starting
10 the cell. This increase of time is disadvantageous not only because of the delay involved, but also because during the melting period the graphite connectors are carrying all the current as cathodes in direct contact
15 with the bath, thus subjecting them to attack and consequent injury thereby. As the anode alloy is being deposited in the cell, or immediately after, the graphite connectors are raised, leaving them dipping into the
20 floating electrolyte to the extent of only an inch or two.

A layer of molten aluminum, preferably the purest available, is now deposited on the layer of fused electrolyte. By preference
25 this is done by pouring the metal slowly on an asbestos board, as 35, Fig. 5, extending over the edge of the cell, so that as the metal runs into the cell it will meet the electrolyte at an acute angle and hence
30 will not be carried down into contact with the impure anode metal or alloy. During this addition of the cathode metal the graphite electrodes are again raised so that at the end of the operation they dip only into the
35 molten cathode metal, represented by the layer 36, Fig. 5, and become mere connectors between the cathode and the negative busbar 31, rather than cathodes in contact with the bath. The asbestos board or other
40 appliance used in running the cathode metal into the cell is removed as soon as possible.

As the cathode metal is added, molten bath begins to creep up by capillary action between the steel shell and the adjoining
45 cathode metal, and as a result of the cooling due to the water jackets freezes there to form the side-lining or crust 32, Fig. 1, above the lower portion shown at 32^a in Figs. 3, 4 and 5. The formation of the crust to the desired
50 thickness can be greatly accelerated by depositing solid electrolyte in powdered form (with or without additional alumina) on the inwardly and downwardly sloping sides of the upper shell section 10, so that it
55 works down between the same and the molten aluminum, where molten electrolyte coming up from below by capillary attraction causes it to frit together, thus forming in a short time a sufficiently thick crust having the
60 desired insulating properties.

The cell is now in a condition such as is illustrated in Fig. 1, with the refining process in operation. By the use of my method
65 I have been able to bring the starting period, during which the several molten layers are

established in the cell and the side-lining formed, down to less than 20 minutes for a cell large enough for approximately 1200 pounds of anode alloy, 1500 pounds of electrolyte, and 600 pounds of cathode aluminum, but the time usually runs over a half-hour on account of delays so apt to occur in
70 handling large quantities of different molten materials at temperatures in the neighborhood of 1000° C.

The preliminary heating of the carbon bottom of the cell is advantageous in preventing cracking of the lining and spattering of the fluid bath as it is poured in, both of which may occur if the bath is poured
80 upon the cold lining. The spattering is very apt to be dangerous if for any reason a little moisture has accumulated at any point in the lining. If electrolyte in the molten state is not available the desired layer may be
85 formed by melting the powdered mixture in the cell bottom by the heat evolved at the points of contact with the graphite electrodes, but the time, labor, and graphite consumption are then much greater.

While I have described my process in conjunction with a method of refining aluminum it can be used to advantage with the electrolytic refining of other metals with a
90 suitable electrolyte. Nor is the invention limited to the features herein specifically described, since it can be carried out in other ways without departure from its spirit as defined by the appended claims.

I claim:

1. The process of putting an electrolytic cell in condition for electrolytic refining of metal, comprising establishing in the cell a layer of molten electrolyte and thereafter
100 two layers of molten metal in succession, differing in density from each other and from the electrolyte; freezing on the sides of the cell from the electrolyte layer a crust adapted to form part of a side-lining, before the
105 second metal layer is established; and thereafter completing the side-lining.

2. The process of putting an electrolytic cell in condition for electrolytic refining of metal, comprising establishing in the cell in suitable order upper and lower molten
115 metallic layers of different densities and an intermediate layer of fused electrolyte of intermediate density, and before the second metallic layer is established freezing from the electrolyte on the sides of the cell a crust
120 adapted to serve as part of a side-lining; and after the said second metallic layer is established, completing the formation of the side lining.

3. The process of putting an electrolytic cell in condition for electrolytic refining of metal, comprising establishing in the bottom of the cell a body of molten electrolyte adequate in amount to form a layer of suitable
125 thickness for the subsequent refining opera- 130

tion; establishing in the cell a body of molten metal denser than the electrolyte and in amount adapted to raise the electrolyte to a position suitable for the subsequent refining operation; freezing on the sides of the cell from the electrolyte layer in contact therewith, a crust adapted to form part of a side-lining; establishing on the electrolyte layer a layer of molten metal less dense than the electrolyte and of a thickness suitable for the subsequent refining operation; and after the last-mentioned metallic layer is established completing the formation of the side-lining.

4. The process of putting an electrolytic cell in condition for electrolytic refining of metal by a method in which current is passed between a lower layer of molten alloy as anode and an upper layer of molten metal as cathode through an intermediate layer of fused electrolyte, comprising establishing in the cell a body of fused electrolyte of greater density than the cathode metal and of lower density than the anode alloy and in amount suitable for the subsequent refining operation; depositing in the cell molten anode alloy in amount sufficient to raise the electrolyte to its operative position; cooling the cell walls in contact with the electrolyte and freezing a crust therefrom on said walls; depositing on the electrolyte a body of molten cathode metal in amount suitable for the subsequent refining operation; and causing additional crust to form on the sides of the cell, between the same and the molten cathode metal.

5. The process of putting an electrolytic cell in condition for electrolytic refining of metal, comprising depositing in the cell, one after another in suitable order, molten bodies of anode metal, cathode metal and electrolyte in amounts suitable for the refining operation and having densities adapted to give the electrolyte a position between the two metal bodies, and while the said molten bodies are being established maintaining the mobility of the cell contents by passing current therethrough; and forming on the sides of the cell a crust composed at least in part of electrolyte frozen thereon to insulate the electrolyte and the upper body of metal from the cell walls.

6. The process of putting an electrolytic cell in condition for electrolytic refining of metal, comprising establishing in the cell a body of molten electrolyte in amount adapted for the subsequent refining operation, establishing below the body of electrolyte a body of molten anode metal of greater density and in amount adapted to raise the electrolyte to its operative position; establishing on the electrolyte a body of molten cathode metal of less density than the electrolyte and in amount suitable for the refining operation; maintaining the cell contents

in molten condition by passing current therethrough while the several molten bodies are being established; and forming between the cell walls and the bodies of electrolyte and cathode metal an insulating lining composed at least in part of frozen electrolyte.

7. The process of putting an electrolytic cell in condition for electrolytic refining of metal, comprising establishing in the cell a layer of molten electrolyte and thereafter in succession two layers of molten metal differing in density from each other and from the electrolyte, forming on the sides of the cell between the same and the electrolyte and cathode metal an insulating side-lining composed at least in part of electrolyte frozen on the cell walls; and maintaining the mobility of the molten contents of the cell by passing current therethrough.

8. The process of putting an electrolytic cell in condition for electrolytic refining of metal, comprising establishing in the cell in suitable order upper and lower molten metallic layers of different densities and an intermediate layer of fused electrolyte of intermediate density, and before the second metallic layer is established freezing from the electrolyte on the sides of the cell a crust adapted to serve as part of a side-lining; completing the formation of the side lining after the second metallic layer is established; and maintaining the mobility of the cell contents during establishment of said layers by passing current therethrough.

9. The process of putting in condition for operation an electrolytic refining cell having a refractory bottom, comprising preheating the bottom, depositing in the cell a layer of molten electrolyte and thereafter two layers of molten metal in succession, differing in density from each other and from the electrolyte; forming on the sides of the cell from the electrolyte layer a crust adapted to form part of the side-lining, before the second metal layer is established; and thereafter completing the side-lining.

10. The process of putting in condition for operation an electrolytic refining cell having a refractory conducting bottom, comprising preheating the bottom, depositing in the cell in suitable order upper and lower molten metallic layers of different densities and an intermediate layer of fused electrolyte of intermediate density, and before the second metallic layer is established freezing from the electrolyte on the sides of the cell a crust adapted to serve as part of a side-lining; and after the said second metallic layer is established, completing the formation of the side lining; while maintaining mobility of the successive layers by passing current therethrough.

11. The process of putting an electrolytic cell in condition for electrolytic refining of

metal, comprising establishing in the bottom of the cell a body of molten electrolyte; pouring into the cell a body of molten metal denser than the electrolyte, the pouring being slow, so as to raise the electrolyte gradually to a position suitable for the subsequent refining operation and avoid mixing the metal therewith; freezing on the sides of the cell from the electrolyte layer in contact therewith, a crust adapted to form part of a side lining; establishing on the electrolyte layer a layer of molten metal less dense than the electrolyte and of a thickness suitable for the subsequent refining operation; and after the last-mentioned metallic layer is established completing the formation of the side-lining.

12. The process of putting an electrolytic cell in condition for electrolytic refining of metal, comprising preheating the bottom of the cell, depositing on the bottom of the cell a body of molten electrolyte adequate in amount to form a layer of suitable thickness for the subsequent refining operation; pouring slowly through the body of electrolyte a body of molten metal denser than the electrolyte and in amount adapted to raise the latter to a position suitable for the subsequent refining operation; freezing on the sides of the cell from the electrolyte layer in contact therewith, a crust adapted to form part of a side-lining; establishing on the electrolyte layer a layer of molten metal less dense than the electrolyte and of a thickness suitable for the subsequent refining operation; and after the last-mentioned metallic layer is established completing the formation of the side-lining.

13. The process of putting an electrolytic cell in condition for electrolytic refining of metal, comprising preheating the bottom of the cell, depositing on the bottom of the cell a body of molten electrolyte adequate in amount to form a layer of suitable thickness for the subsequent refining operation; pouring slowly through the body of electrolyte a body of molten metal denser than the electrolyte and in amount adapted to raise the latter to a position suitable for the subsequent refining operation; freezing on the sides of the cell from the electrolyte layer in contact therewith, a crust adapted to form part of a side-lining; pouring on the electrolyte layer, slowly and in a stream inclined thereto, a body of molten metal less dense than the electrolyte and of a thickness suitable for the subsequent refining operation; and after the last-mentioned metallic layer is established completing the formation of the side-lining.

14. The process of putting an electrolytic cell in condition for electrolytic refining of metal, comprising establishing in the cell a

layer of molten electrolyte and thereafter two layers of molten metal in succession, differing in density from each other and from the electrolyte; and forming on the sides of the cell, by freezing from the electrolyte layer with the addition of electrolyte material in solid form, a side-lining between the cell walls and the electrolyte and upper metallic layer.

15. The process of putting an electrolytic cell in condition for electrolytic refining of metal, comprising establishing in the cell a layer of molten electrolyte and thereafter two layers of molten metal in succession, differing in density from each other and from the electrolyte; forming on the sides of the cell, by freezing from the electrolyte layer with the addition of electrolyte material in solid form, a side-lining between the cell walls and the electrolyte and upper metal layer, and maintaining mobility of the cell contents by passing current there- through.

16. The process of putting an electrolytic cell in condition for electrolytic refining of metal, comprising preheating the bottom of the cell; pouring into the cell, one after another in suitable order and at rates adapted to prevent mixing, molten bodies of anode metal, cathode metal and electrolyte in amounts suitable for the refining operation and having densities adapted to give the electrolyte a position between the two metal bodies, and while the said molten bodies are being established maintaining the mobility of the cell contents by passing current there- through; and forming on the sides of the cell a crust composed at least in part of electrolyte frozen thereon to insulate the electrolyte and the upper body of metal from the cell walls.

17. The process of putting an electrolytic cell in condition for electrolytic refining of metal, comprising preheating the bottom of the cell; pouring into the cell, one after another in suitable order and at rates adapted to prevent mixing, molten bodies of anode metal, cathode metal and electrolyte in amounts suitable for the refining operation and having densities adapted to give the electrolyte a position between the two metal bodies, and while the said molten bodies are being established maintaining the mobility of the cell contents by passing current there- through; and freezing on the sides of the cell a crust composed of electrolyte and forming thereby with additional solid material a lining to insulate the electrolyte and the upper body of metal from the cell walls.

In testimony whereof I hereto affix my signature.

DONALD HEATH TILSON.