(No Model.) 4 Sheets—Sheet 1.

C. KELLNER.

METHOD OF AND APPARATUS FOR EFFECTING ELECTROLYSIS.

No. 586,729. Patented July 20, 1897.

Fig. 1

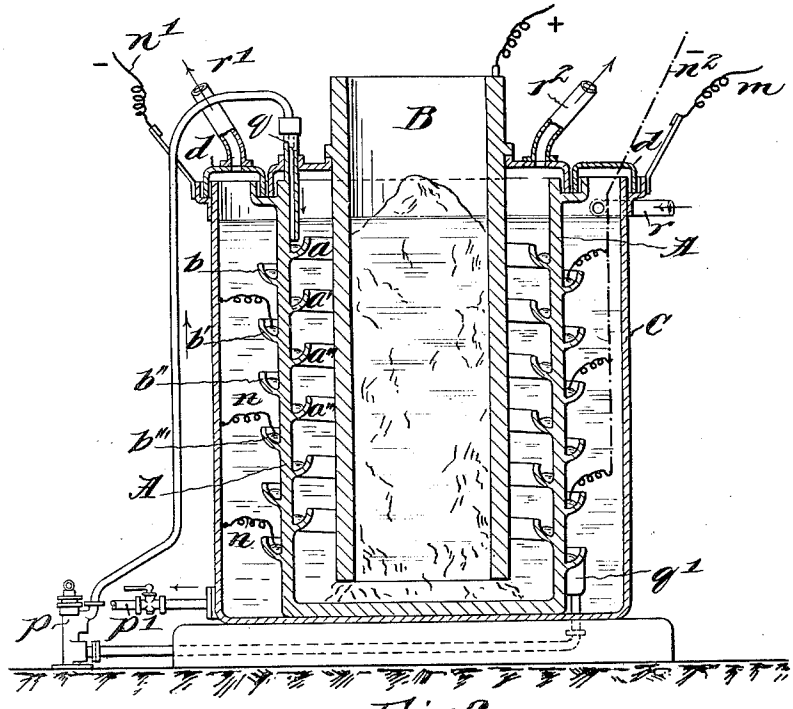
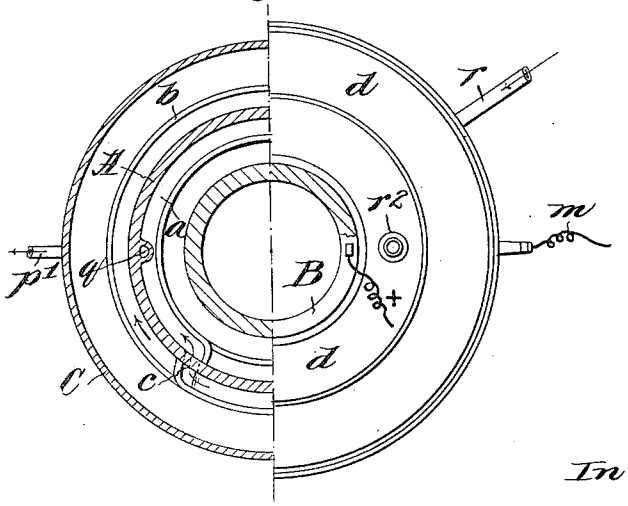


Fig. 2.



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(No Model.) 4 Sheets—Sheet 2.

C. KELLNER.

METHOD OF AND APPARATUS FOR EFFECTING ELECTROLYSIS.

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Fig. 3.

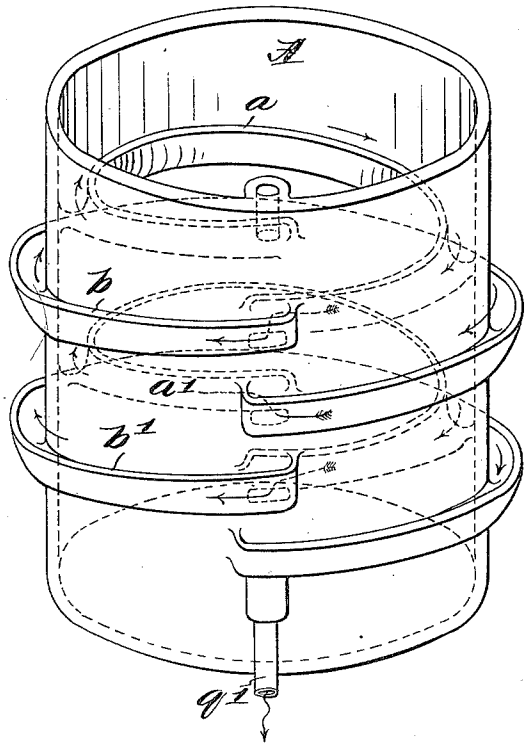


Fig. 4.

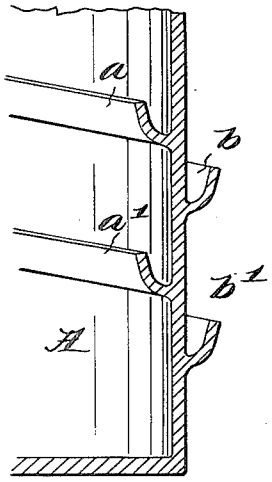
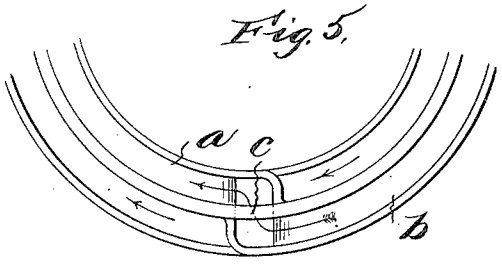


Fig. 5.



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METHOD OF AND APPARATUS FOR EFFECTING ELECTROLYSIS.

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Fig. 7

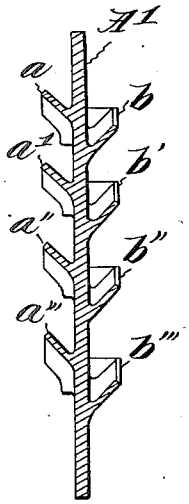


Fig. 6.

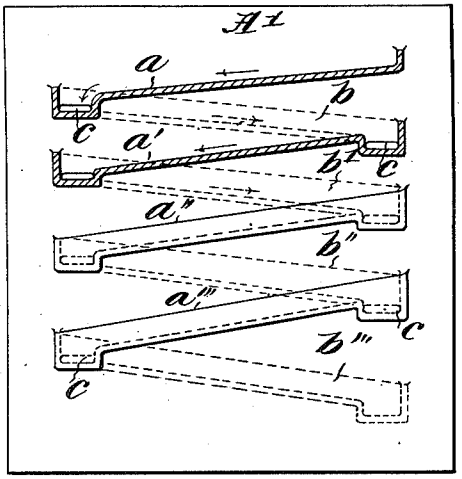


Fig. 8.

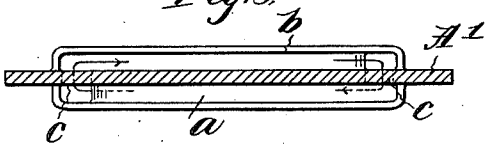
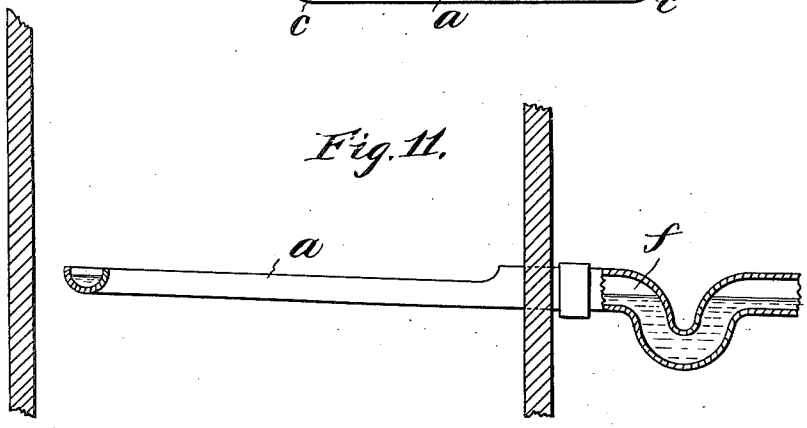


Fig. 11.



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METHOD OF AND APPARATUS FOR EFFECTING ELECTROLYSIS.

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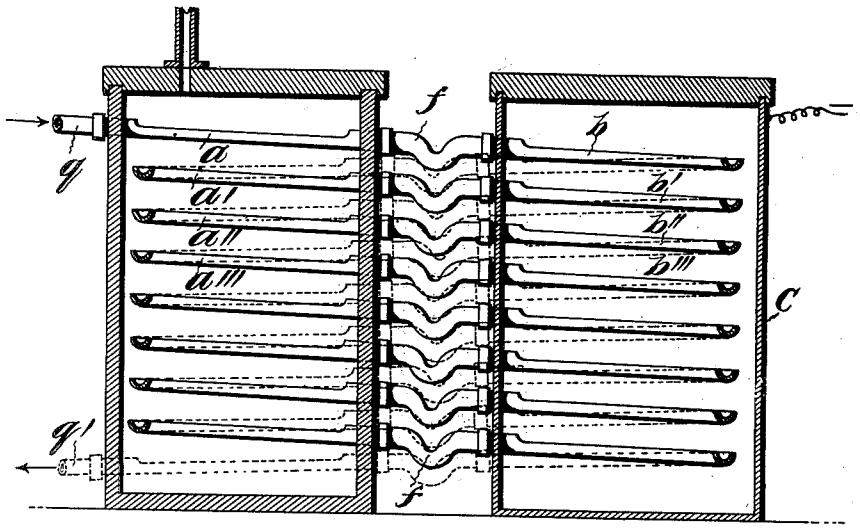
Fig. 10.



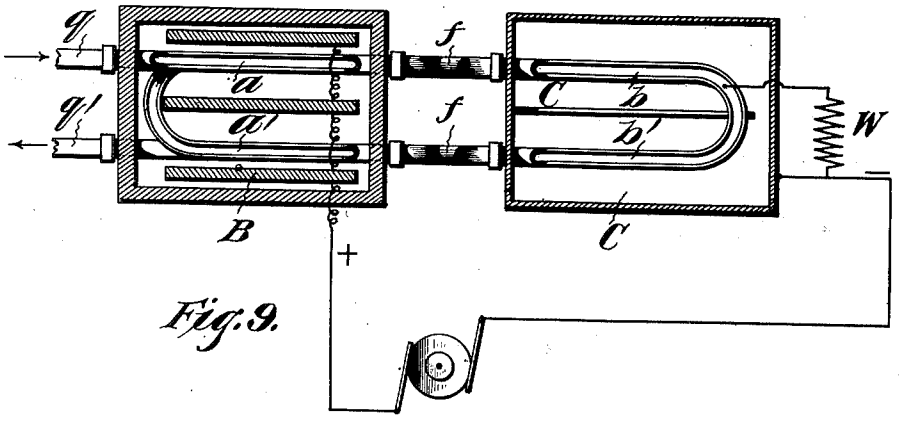


Fig. 9.

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CARL KELLNER, OF VIENNA, AUSTRIA-HUNGARY.

METHOD OF AND APPARATUS FOR EFFECTING ELECTROLYSIS.

SPECIFICATION forming part of Letters Patent No. 586,729, dated July 20, 1897.

Application filed February 24, 1896. Serial No. 580,569. (No model.) Patented in France December 15, 1894, No. 243,672; in Belgium December 15, 1894, No. 113,221; in Italy December 31, 1894, XXIX, 37,828, and LXXIV, 179; in Austria January 17, 1895, No. 45/208; in Hungary February 28, 1895, No. 2,255; in Switzerland July 4, 1895, No. 10,558, and in Norway July 16, 1895, No. 4,439.

To all whom it may concern

Be it known that I, CARL KELLNER, a subject of the Emperor of Austria-Hungary, residing at Vienna, in the Province of Lower Austria, in the Empire of Austria-Hungary, have invented certain new and useful Improvements in the Method of and Apparatus for Effecting Electrolysis, (for which patents have been obtained in the following countries, to wit: Austria, dated January 17, 1895, No. 45/208; Hungary, dated February 28, 1895, No. 2,255; France, dated December 15, 1894, No. 243,672; Belgium, dated December 15, 1894, No. 113,221; Italy, dated December 31, 1894, XXIX, 37,828, and LXXIV, 179; Switzerland, dated July 4, 1895, No. 10,558, and Norway, dated July 16, 1895, No. 4,439;) and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same, reference being had to the accompanying drawings, and to letters of reference marked thereon, which form a part of this specification.

As is well known, the vertical arrangement of electrolytic apparatus is for many reasons to be preferred to the horizontal arrangement. This is especially the case with apparatus in which mercury is employed as an electrode, because, first, it is difficult to place and maintain large and heavy apparatus horizontal with such accuracy as to cause the bottom to be everywhere uniformly covered with a thin layer of this expensive metal; second, it is difficult to act electrolytically upon large horizontal surfaces uniformly, and experience shows that an amalgam of an alkali metal decomposes the water of the electrolyte at the places of small current density, which in the case of the electrolysis of the chlorids of the alkali metals causes the formation of hypochlorites; third, the output capacity of horizontal apparatus is restricted by difficulties in respect of construction and material, many contacts, large space, and numerous apparatus being required; fourth, the surface of the mercury, which alone is effective or operative, is rendered impure by the anodes arranged above it; fifth, in practical working it is very inconvenient to keep large quantities of mercury in constant uniform movement.

It has heretofore been proposed to employ mercury in a vertical or inclined form—as a cathode, for instance—by causing it to trickle in thin sheets or streams down over vertical or slightly-inclined amalgamated metallic surfaces constituting the cathode or by drawing amalgamated metallic bodies, bands, and strips of sheet metal through mercury; but all these apparatus are so complicated and their output is so small as to render them unfit for use for working on a large scale.

Now the present invention is designed to provide means for enabling the complete decomposition of metallic chlorids to be effected electrolytically with the practically complete utilization of the electrochemical equivalent of energy by means of vertically-arranged, extremely simple, durable, and reliably-working apparatus without the use of a porous diaphragm or partition.

According to this invention the mercury cathode is employed in the form of narrow strips, which are formed by a system of channels and are compelled to circulate in a helical or zigzag path or paths about the anode or anodes while they are being continuously freed in a cell separated from the decomposing-chamber from the cation they have taken up in their course. By employing this method it has also been rendered possible to construct apparatus of any desired output capacity.

The quantity of mercury required is small in consequence of the high current density that is attainable therewith, and the raising apparatus or operation is simple because it is sufficient, in the case of an apparatus however large, to raise up to the initial convolution of the helical path only that quantity of mercury which is requisite for a single convolution of the helix. In carrying this method into practice the apparatus illustrated by way of example in a number of modified forms in the accompanying drawings may be employed.

Figure 1 illustrates in vertical section, Fig. 2 partly in plan and partly in horizontal section, an apparatus constructed of cylindrical shape. Figs. 3 to 5 are respectively a perspective view, a part vertical section, and a part horizontal section showing a cylinder pro-

vided with helical channels for guiding the mercury strip or stream. Figs. 6, 7, and 8 are respectively an elevation partly in section, a vertical section, and a horizontal section illustrating another construction of apparatus of flat shape adapted to be inserted into existing electrolytic apparatus in place of a diaphragm. Figs. 9 and 10 show, respectively, in horizontal and vertical section another arrangement of apparatus in which the strip-like layer of mercury, in contradistinction to the two forms of apparatus shown in Figs. 1 to 8, is subjected to action or influence on both sides, (as "irradiated" from both sides,) and is consequently adapted to work with a large current density. Fig. 11 shows partly in elevation and partly in section a portion of the channel used in the apparatus shown in Figs. 9 and 10.

In the apparatus illustrated in Figs. 1 to 5 A is a cylinder, composed of material such as porcelain or stoneware, provided with numerous helical channels *a a' a'' b b' b''*, (of which only a few are shown for the sake of clearness,) through which the mercury flows in the form of a stream, the parts of the mercury stream in the several channels constituting strips. The channels are arranged on the cylinder A, Fig. 3, in such a manner that the first, third, fifth, and so on convolutions—that is to say, the channels forming the odd-numbered convolution of the helix—are situated on the inner surface of the cylinder, while the channels forming the second, fourth, sixth, and so on, or even-numbered convolution, are situated on the outer surface of the cylinder. The internal channels situated in the decomposing-cell communicate with the external channels situated in the forming-cell each by means of an opening or slit *c*, formed in the wall of the cylinder.

In the cylinder A, to the uppermost channel *a* of which the mercury is supplied through a pipe *q*, there is inserted a suitable anode (or anodes) B, preferably of cylindrical shape, which is filled with the solid salt to be decomposed, so that this salt cannot enter into the mercury-channels, but by passing from below the anode into the electrolyte around the same will become dissolved therein and so maintain the strength thereof. The whole is arranged in a vessel C, which contains the substance (water or other fluid reagent) with which the separated cation is to be combined and is closed by a cover *d*.

r is the inlet-pipe for the liquid reagent, and *r'* and r^2 are gas-exit pipes.

The anode B is connected to the positive pole of an electric generator and the mercury is connected with the negative pole thereof.

As the resistance of the long stream of mercury, with the considerable current consumption, would be very appreciable, it is advisable to connect the stream of mercury at various points in its length with the negative pole of the electric generator. For this purpose the vessel C is made of metal—for example, iron—and is connected electrically at various points with the mercury by means of the wires *n*, the vessel itself being connected to a wire *n'*, as shown on the left-hand side of Fig. 1, by which it is placed in electrical connection with the negative pole of the electric generator; but if electricity produced by the combination of the cation dissolved in the mercury cathode with the liquid reagent in the vessel C is to be utilized then, as shown on the right-hand side of Fig. 1, the wires *n* are connected to form another common return-lead n^2 to the negative pole of the electric generator, another lead *m* extending from the vessel C. The mercury in the external channels and the vessel form in this case the electrodes of a secondary element which can be advantageously used for supplying current to another electrolytic apparatus or for relieving the main source of current-supply.

If it is mainly desired to effect a decomposition of the mercury amalgam that shall be capable of regulation, all the mercury strips are again connected by a lead with the negative pole of the dynamo-machine, and into this lead there is included a resistance W, Fig. 9, and beyond the latter a connection is made with the conducting vessel C. In this way there is formed a short-circuited element which promotes the formation of caustic soda. The efficiency of this element—that is to say, the speed of the decomposition of the amalgam—may be regulated by varying the resistance.

The mode of operation of the apparatus is as follows: Assuming, for example, that common salt is to be decomposed with the object of producing simultaneously by electrolysis caustic soda and chlorin gas, then a solution of common salt is placed in the decomposing vessel A and water in the combining vessel C, and mercury is poured into the topmost inner channel *a*. As soon as the electric circuit is completed sodium will be separated from the solution of common salt contained in the decomposing vessel and will unite with the mercury cathode, but during the passage of the mercury amalgam through the second helical convolution *b*, situated on the outside of the vessel A, the above-mentioned sodium will combine with the water in the combining vessel, with formation of caustic soda and liberation of hydrogen. The mercury freed from the sodium then passes at once into the next inner helical convolution *a'*, again amalgamates with sodium, carries the same into the outer helical convolution *b'* in the combining vessel, where it yields up the sodium as before, and so on, passing finally out of the apparatus in a pure condition by a pipe *q'* to a pump *p* or other suitable raising device, by which it is again delivered to the pipe *q*, and thus to the topmost inner channel *a* for reuse.

The concentrated solution of caustic soda is drawn off from the vessel C through a pipe *p'*. If instead of water a solution of sodium

nitrate be used in the combining vessel, ammonia-gas will be liberated instead of hydrogen. The hydrogen or ammonia, as the case may be, escapes through the pipe r', while the chlorin escapes through the pipe r^2, the gases being conducted by these pipes to the place where they are to be utilized.

The hereinbefore-described arrangement of vessel A with mercury-channels serves to provide a fluid-tight division between the interiors of the decomposing and combining vessels; but in cases where no value will be attached to this arrangement there may be employed in place of the cylinder A an insulating-wall A′ for separating the two spaces, as shown in Figs. 6, 7, and 8. This wall is provided on both sides with the oppositely-inclined channels *a a′ b b′*, that are connected together by means of slots *c*, so that the mercury flows along a flattened helical or zigzag path extending alternately through the decomposing-space and the combining-spaces. This arrangement is especially suitable for use in existing electrolytic apparatus which work with diaphragms, because it is merely necessary to insert the wall A′ with channel in place of the diaphragm.

In the case of very large apparatus it will be advantageous to employ the construction of apparatus shown in Figs. 9, 10, and 11. In this arrangement the channel portions *a a′* and *b b′* are arranged, respectively, in separate decomposing and combining vessels, the said channel portions being connected together by means of bent pipes *f*, situated outside of and between the said vessels.

Of course it will be understood that the channels *a a′*, &c., and *b b′*, &c., are connected to form a continuous coil-like structure, the channels *a b* leading into channels *a′ b′*, the latter into channels *a″ b″*, and so on throughout the series, as shown in part in Figs. 9 and 10, in which last-named figure two of the channels connected by pipe *f* are shown connected with the last two channels of the series that lead to exit-pipe *q′*, which may be connected by a pump or other raising apparatus with the supply-pipe *q″*.

In the construction described the mercury entering at *q* flows continuously, or substantially so, and alternately from the decomposing vessel to the combining vessel from top downward and out at *q′*. Such mercury as it flows through the open channels or portions *a b a′ b′*, &c., of the channeled conduit comes in contact with the electrolyte and the solvent in said decomposing and combining vessels, respectively, in the presence in the former vessel of two electrodes of opposite polarity arranged in the decomposing vessel on opposite sides and intermediate of the conduit convolutions, as shown, so that the mercury is caused to flow between electrodes of opposite polarity, and is in this manner subjected to the action of the electric current from opposite sides, (irradiated,) whereby but one-half the quantity of mercury necessary in the apparatuses hereinbefore referred to will be required, while the output will be the same.

I claim—

1. In a process for the electrolytic decomposition of salts of metals capable of combining with mercury, passing an electric current through a solution of such salt, to a mercury cathode flowing uninterruptedly from a higher to a lower level and before reaching such lower level flowing alternately and repeatedly out of contact with the salt solution into contact with an agent capable of decomposing the compound or amalgam formed, for the purpose set forth.

2. In a process for the electrolytic decomposition of salts of metals capable of combining with mercury, passing an electric current through a solution of such salt to a mercury cathode flowing uninterruptedly from a higher to a lower level and before reaching such lower level and while under the influence of the electric current flowing alternately and repeatedly out of contact with the salt solution into contact with an agent capable of decomposing the compound or amalgam formed while under the influence of such electric current, for the purpose set forth.

3. In a process for the electrolytic decomposition of salts of metals capable of combining with mercury, passing an electric current through a solution of such salt to a mercury cathode flowing uninterruptedly from a higher to a lower level and before reaching such lower level and while under the influence of the electric current flowing alternately and repeatedly out of contact with the salt solution into contact with an agent capable of decomposing the compound or amalgam formed while under the influence of such electric current, for the purpose set forth.

4. In a process for the electrolytic decomposition of salts of metals capable of combining with mercury, passing an electric current through a solution of such salt to a mercury cathode flowing in a contracted or ribbon-like streamlet uninterruptedly from a higher to a lower level and before reaching such lower level flowing repeatedly out of contact with the salt solution into contact with an agent capable of decomposing the compound or amalgam formed, for the purpose set forth.

5. In a process for the electrolytic decomposition of salts of metals capable of combining with mercury, passing an electric current through a solution of such salt to a mercury cathode flowing in a contracted or ribbon-like streamlet uninterruptedly from a higher to a lower level and before reaching such lower level, flowing while under the influence of the electric current alternately and repeatedly out of contact with the salt solution into contact with an agent capable of decomposing the compound or amalgam formed, for the purpose set forth.

6. In a process for the electrolytic decomposition of salts of metals capable of combining with mercury, passing an electric current through a solution of such salt to a body of mercury included in the electric circuit, and moving a plurality of contracted or ribbon-like streamlets of said mercury alternately and repeatedly through said solution and through an agent capable of decomposing the compound or amalgam formed, for the purpose set forth.

7. In a process for the electrolytic decomposition of salts of metals capable of combining with mercury, passing an electric current through a solution of such salt to a mercury cathode flowing uninterruptedly from a higher to a lower level and before reaching such lower level flowing alternately and repeatedly out of contact with said solution into contact with an oxidant and solvent of the cation in the compound or amalgam formed and using the mercury of said compound or amalgam as an electrode for a primary element, for the purpose set forth.

8. In a process for the electrolytic decomposition of salts of metals capable of combining with mercury, passing an electric current through a solution of such salt, to a body of mercury included in the electric circuit, moving a plurality of contracted or ribbon-like streamlets of said mercury simultaneously and alternately through an oxidant and solvent of the cation in the compound or amalgam formed, and using the mercury in said compound or amalgam as an electrode for a primary element, for the purpose set forth.

9. In a process for the electrolytic decomposition of salts of metals capable of combining with mercury, passing an electric current through a solution of such salt to a mercury cathode flowing in a contracted or ribbon-like streamlet in a zigzag direction from a higher to a lower level and before reaching such lower level flowing alternately and repeatedly out of contact with said solution into contact with an agent capable of decomposing the compound or amalgam formed, for the purpose set forth.

10. An electrolytic apparatus comprising two compartments, a fixed anode in one of them, a mercury cathode, and means for causing said cathode to uninterruptedly flow from a higher to a lower level alternately and repeatedly from one compartment to the other before reaching such lower level.

11. A partition for electrolytic apparatus provided on both faces with a series of superposed channels, those on one face being inclined in a direction opposite to that of the channels on the other face, and openings in said partition leading from the lowest point of a channel on one of its faces to the highest point of a channel on the opposite face to form a continuous channel, for the purpose set forth.

12. An electrolytic apparatus comprising two compartments fixed electrodes for each of said compartments, a second electrode for both compartments formed of mercury, in combination with means for continuously moving the mercury in a downward direction alternately and repeatedly from one compartment to the other, and electrical connections connecting the mercury in one of the compartments to the fixed electrode for said compartment, for the purpose set forth.

13. An electrolytic apparatus comprising two concentrically-arranged vessels, the inner vessel provided on both faces with downwardly-inclined channels connected in series to form a continuous channel from the upper to the lower end of said vessel, a pump whose force and suction pipes are respectively connected with the initial and terminal of said channel, a body of mercury adapted to circulate through said channel and a cylindrical fixed electrode extending nearly to the bottom of the inner vessel; in combination with electric connections respectively connecting the mercury in the channel portions in the outer face of the inner vessel, and the fixed electrode in said inner vessel with opposite poles of a source of electricity, substantially as and for the purpose set forth.

14. An electrolytic apparatus comprising two compartments each provided with downwardly-inclined and interconnected channel-sections forming a continuous channel leading alternately from one compartment to the other, a body of mercury in said channel, and a pump whose force and suction pipes are respectively connected with the initial and terminal of said channel, whereby the mercury therein is caused to continuously flow in a downward direction through the channel, and alternately from one compartment to the other; in combination with a fixed electrode in one of said compartments connected with one pole of a source of electricity, electrical conductors connecting the mercury in the channel-sections of the other compartment with the other pole of said source of electricity, and a resistance interposed in the last-named connections, for the purpose set forth.

15. In a process for the electrolytic decomposition of salts of metals capable of combining with mercury, passing an electric current through a solution of such salt to a mercury cathode flowing from a higher to a lower level alternately and repeatedly out of contact with said solution into contact with an agent capable of decomposing the compound or amalgam formed, and short-circuiting the amalgam when brought into contact with said decomposing agent with a suitable cathode, for the purpose set forth.

In testimony whereof I affix my signature in presence of two witnesses.

CARL KELLNER.

Witnesses:
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