Jan. 31, 1961 L. KANDLER ET AL 2,970,095

METHOD AND APPARATUS FOR ELECTROLYTIC DECOMPOSITION OF AMALGAMS

Filed Oct. 3, 1955

5 Sheets-Sheet 1

Fig. 1.

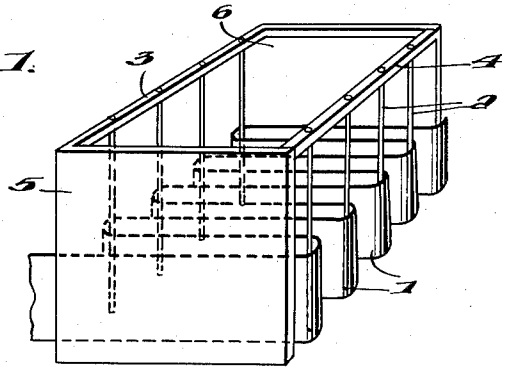


Fig. 2.

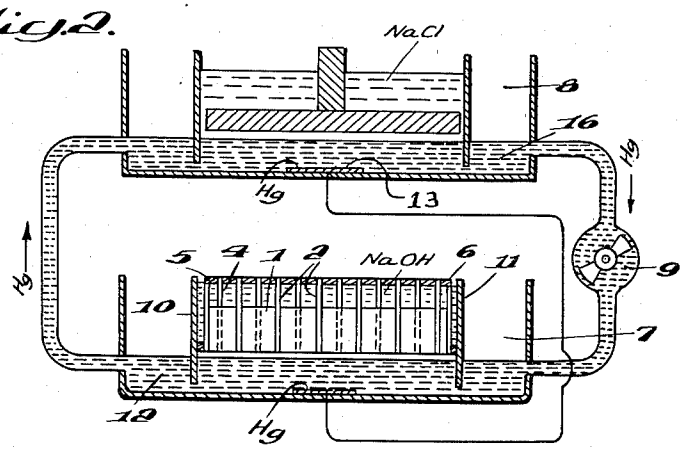
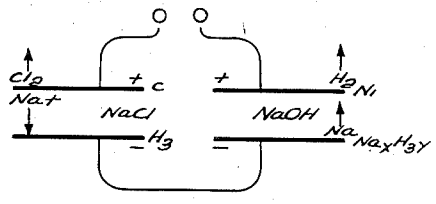


Fig. 3.



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Fig. 12.

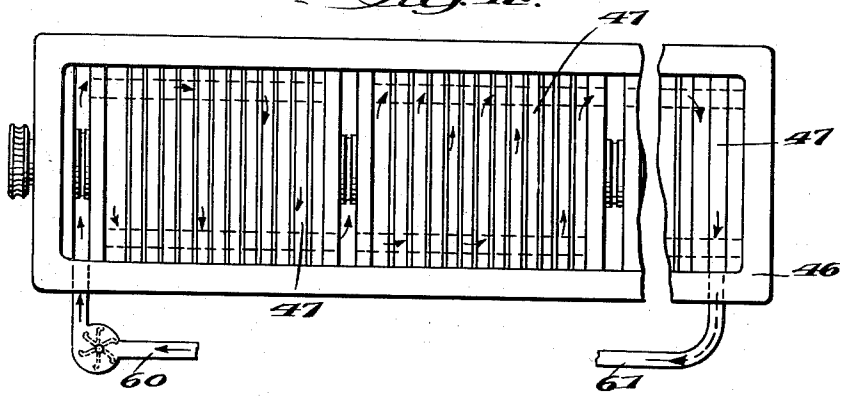


Fig. 13.

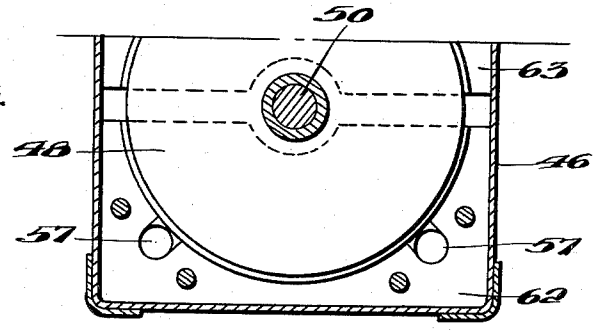


Fig. 4.

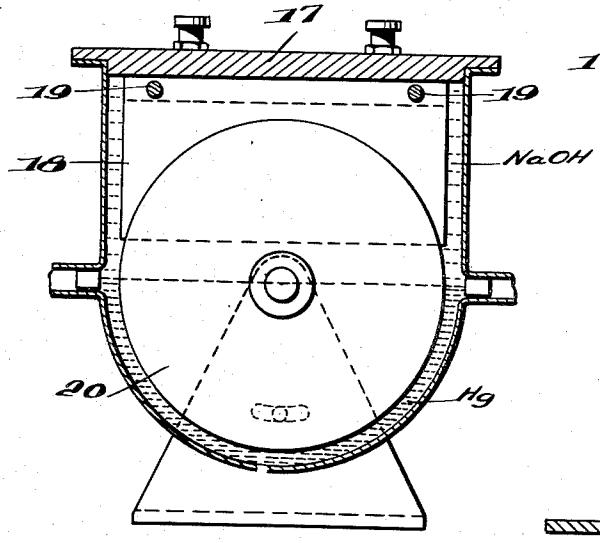
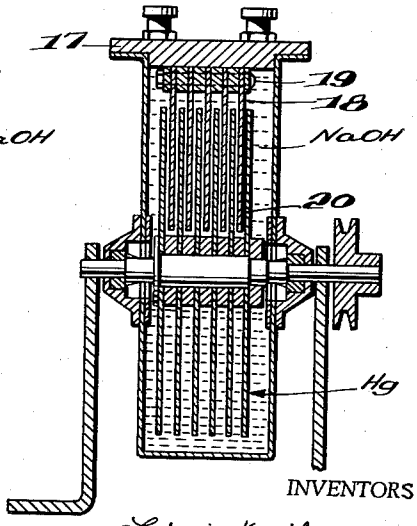


Fig. 5.



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Fig. 6.

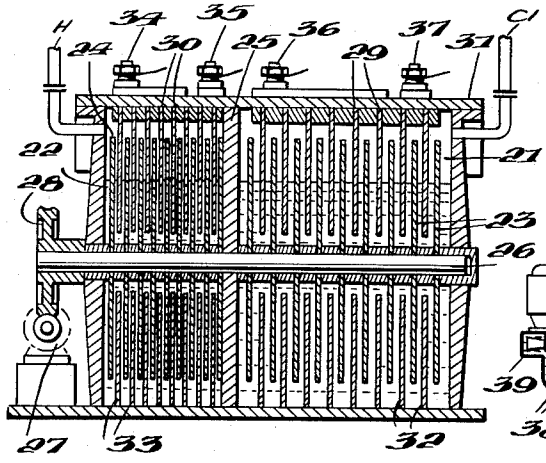
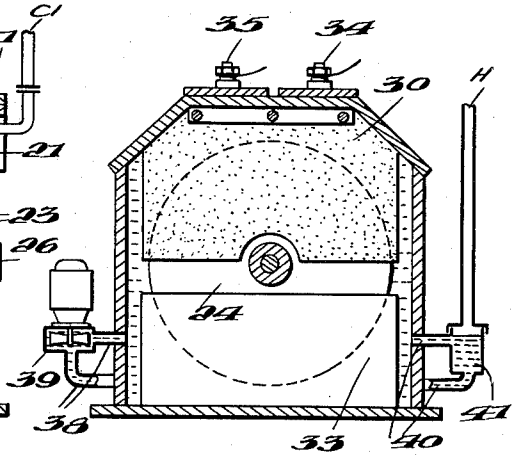


Fig. 7.



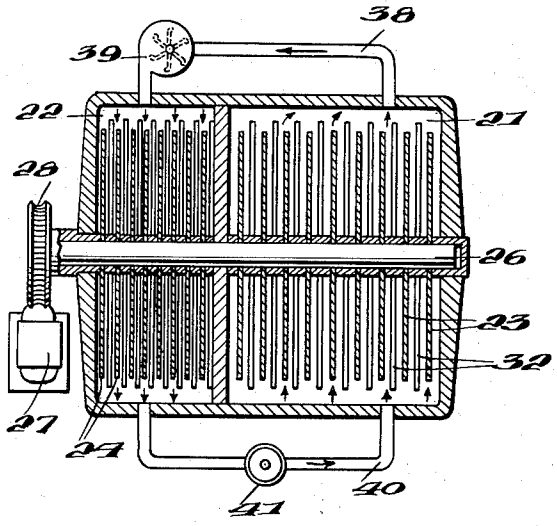


Fig. 8.

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METHOD AND APPARATUS FOR ELECTROLYTIC DECOMPOSITION OF AMALGAMS

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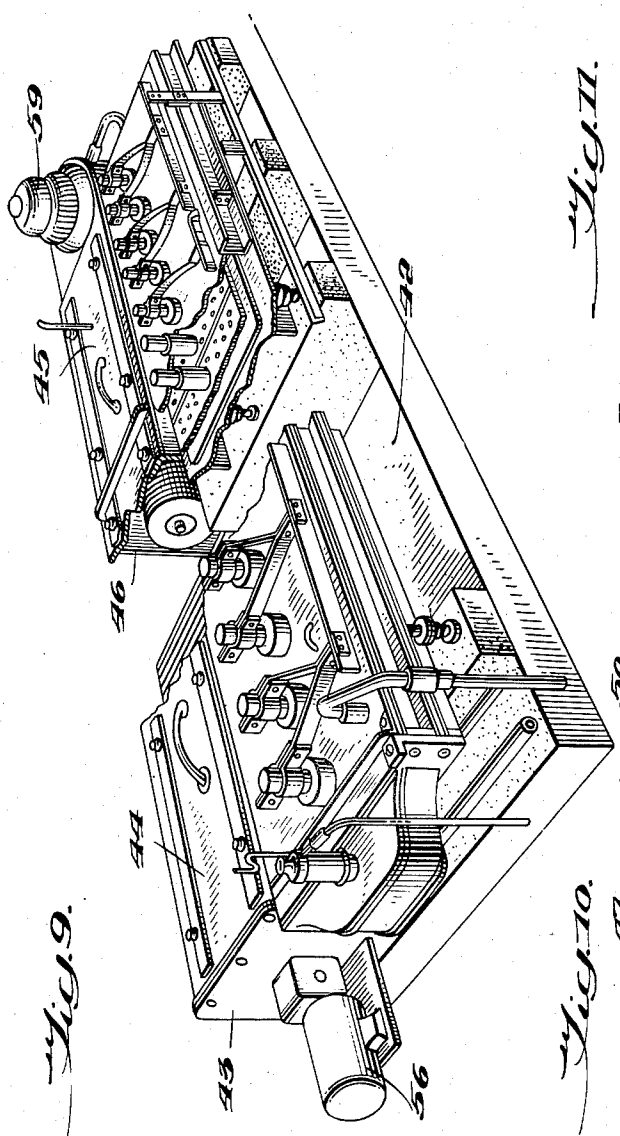


Fig. 9.

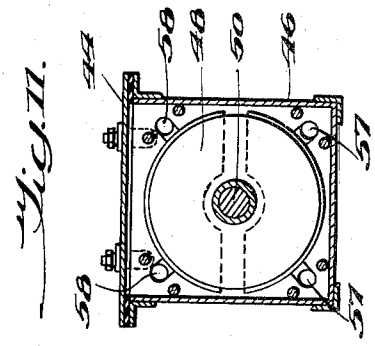


Fig. 11.

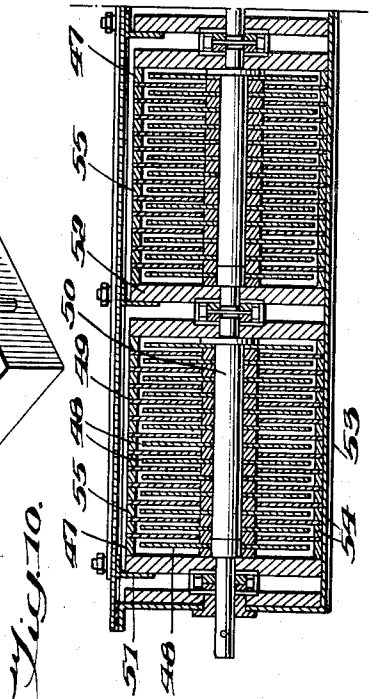


Fig. 10.

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METHOD AND APPARATUS FOR ELECTROLYTIC DECOMPOSITION OF AMALGAMS

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Fig. 14.

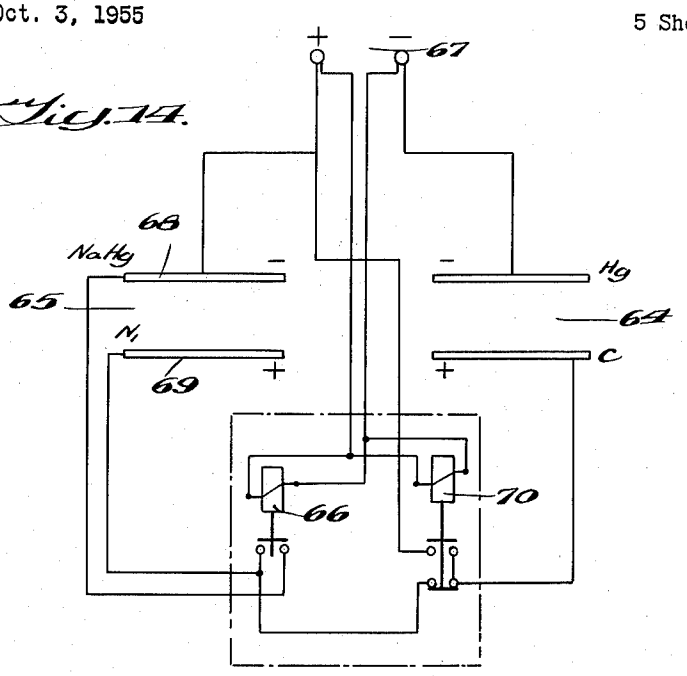
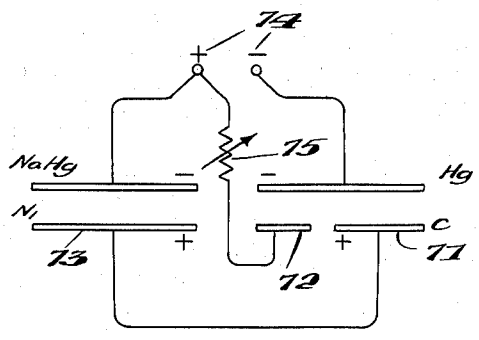


Fig. 15.



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2,970,095

METHOD AND APPARATUS FOR ELECTROLYTIC DECOMPOSITION OF AMALGAMS

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Filed Oct. 3, 1955, Ser. No. 538,126

Claims priority, application Germany Oct. 7, 1954

15 Claims. (Cl. 204—99)

This invention relates to a method and arrangement for the electrolytic decomposition of amalgams. Among the various processes of alkali-chloride electrolysis applied on a large scale the so-called amalgam process proved particularly satisfactory. In this process, mercury is used as a cathode material which binds the alkali metal resulting in the electrolysis of alkali-chloride, in the form of amalgam. In a separate process the alkali amalgam is decomposed again, under formation of alkali lye and hydrogen. The decomposition of amalgam may be effected electrochemically in such a way that either another electrode consisting of iron, nickel or graphite is opposed to the amalgam electrode or the amalgam electrode is brought into direct contact with suitable substances such as graphite or iron.

In the first case, depending on the working conditions, a galvanic cell or an electrolytic cell is produced, while in the second case short-circuited local cells are obtained.

It is an object of the present invention to provide a method and arrangement of the type preferred to which has a reduced demand of energy in relation to the calculated daily capacity of the plant, or an increased capacity without increase of the consumption of energy.

A special object of the invention is to utilize the voltage of the decomposition cell as an additional voltage for the voltage required in the anode chamber.

With these and further objects in view, according to the present invention the electrolytic decomposition of amalgams is effected according to the first one of the above mentioned possibilities, using an amalgam electrode which is opposed to a depolarization electrode, the depolarization electrode having a single potential which at a high current density is more positive than the single potential of the amalgam electrode.

The importance of the alkali-chloride electrolysis according to the present invention will be clear from the following practical example:

At an operating voltage of 4.5 volts, 450,000 kilowatt-hours are required for the daily production of 100 tons of chlorine. If according to the invention 0.5 volt is available additionally from the decomposition element for the voltage required in the amalgam formation chamber, this means a daily of saving of current of about 45,000 kilowatt-hours.

According to the present invention the said advantages are obtained by the generation of an additional voltage in the decomposition element for the voltage required in the amalgam formation chamber, in such a way that the depolarization electrode even at high current densities has a single potential which is more positive than the single potential of the amalgam electrode

The requirements of the method according to the invention can be realized in a favorable manner in a plant known as a horizontal mercury cell, operating with two separate cells, consisting of rubberized iron boxes, one of which forms the amalgam formation chamber while the other one forms the decomposition chamber.

The mercury is passed through the two chambers in a closed cycle, being enriched with metallic sodium in the amalgam formation chamber and then flowing into the decomposition chamber which is lined with roughened iron or graphite slabs, whereby short-circuited local cells are produced which cause the decomposition of the amlagam. The water or the lye is passed over the amalgam in a counter current flow. Thus being impoverished in metallic sodium, the mercury is collected in a space of the amalgam decomposition chamber from which it is conveyed through a pump or the like into the amalgam formation chamber, for repeating the said cyclic course. The current is fed from the negative pole of the source of direct current to the mercury of the amalgam formation chamber through metal slabs embedded in the bottom of the amalgam formation chamber, while the graphite anodes are connected with a positive pole of the source of direct current. In this known plant the short-circuited local cells in the decomposition chamber do not contribute any voltage which could be utilized for the decomposition of the chloride. Such a contribution of voltage according to the invention is possible only if a depolarization electrode is opposed to the amalgam electrode in the decomposition chamber which depolarization electrode has a single potential that is more positive than the single potential of the amalgam electrode.

The requirement according to the invention can be fulfilled in a favorable manner if the depolarization electrode has an effective surface which is a multiple of the geometric area of this surface. Porous sintered electrically conductive substances, for instance nickel powder, iron powder or a mixture of the two powders which are resistant to the electrolytic solution of the decomposition cell, are very suitable for forming such depolarization electrodes with increased effective surface area. Preferably, porous sintered nickel skeletons are used as electrodes which are very thin, like a leaf or foil. Owing to the small thickness of the porous nickel layer, combined with a relatively high mechanical strength, the possibility exists of opposing to the amalgam electrode a nickel electrode whose surface is dimensioned in such a way that an overvoltage of the hydrogen of less than about 0.5 volts results at a current density of more than 15 amperes per $dm.^2$. Owing to the low current density the possibility of polarizing the nickel electrode is small, i.e. even at high current densities a potential difference results between the amalgam electrode and the nickel electrode which develops hydrogen. This potential difference results in the desired reduction of the voltage in the process of total electrolysis in accordance with the invention.

Comparative measurements of the overvoltage of the hydrogen on sintered highly porous nickel electrodes which are as thin as a leaf or foil, have shown the excellent superiority of the said sintered electrodes compared to smooth nickel electrodes and graphite electrodes. On further investigations it has been confirmed that the process according to the invention and the new nickel electrodes belonging thereto offer the possibility of gaining a voltage of about 0.5 volt from the decomposition chamber for the per se known alkali-chloride electrolysis.

The advantage obtainable by using in the decomposition chamber an electrode according to the invention also permits the reaching of higher concentrations of lye than the conventional ones. The reduction of the gain of voltage aimed at according to the invention caused by such higher concentrations of lye is compensated by a reduced consumption of energy when evaporating the lye for concentration thereof.

According to the invention the amalgam electrode in the decomposition chamber acts as a negative electrode of a galvanic cell, and oxidation of this electrode which

may occur if the decomposition chamber is operated as an electrolytic cell, is thus avoided.

Other and further objects, features and advantages of the invention will be pointed out hereinafter and appear in the appended claims forming part of the application.

In the accompanying drawings several now preferred embodiments of the invention are shown by way of illustration and not by way of limitation.

Fig. 1 is a perspective view of a nickel electrode having the invention applied thereto,

Fig. 2 is a diagrammatic sectional view showing the use of the nickel electrode of Fig. 1 in an arrangement and process according to the invention,

Fig. 3 is a diagram of connection of a circuit arrangement adapted for use in a process according to the invention,

Fig. 4 is a cross sectional view of a vertical electrolytic chamber having the invention applied thereto,

Fig. 5 is an axial section thereof,

Fig. 6 is an axial section, on a vertical plane, of a combination of an electrolytic cell having vertical circular disc electrodes rotating about a horizontal axis with a primary cell whose electrodes rotate about a horizontal axis,

Fig. 7 is a cross sectional view of the cell unit shown in Fig. 6,

Fig. 8 is an axial section of the cell unit shown in Fig. 6, on a horizontal plane,

Fig. 9 is a perspective view of an arrangement in accordance with the invention, comprising a horizontal electrolytic trough,

Fig. 10 is a vertical axial section through the trough shown in Fig. 9,

Fig. 11 is a cross sectional view of the trough shown in Fig. 9,

Fig. 12 is a plan view of the trough shown in Fig. 9,

Fig. 13 is a cross sectional view same as Fig. 11, on a larger scale,

Fig. 14 shows a circuit arrangement adapted for use in connection with the cell arrangement in accordance with the invention,

Fig. 15 is a modified circuit arrangement adapted for use in connection with the cell arrangement in accordance with the invention.

Similar reference numerals denote similar parts in the different views.

The depolarization electrode shown in Fig. 1 is formed by a highly porous nickel strip **1** which extends over the carrier bars **2**, being tentered in the form of a serpentine meander. In other words, the strip consists of a plurality of spaced planar portions (i.e., planar elements) connected at their ends to form a continuous serpentine. The bars **2** are secured to strips **3** and **4**. Parts **5** and **6** are metallic end walls serving to stabilize the electrode. The nickel strip **1** is formed by a layer of nickel powder applied by sintering on both sides of a carrier foil in a highly porous form. The total thickness of the highly porous nickel electrode **1** shaped in this manner is about 0.8 mm. The carrier foil of the sintered nickel powder skeleton renders it possible to provide a meander-shaped electrode, whereby the same can be made in one piece, so that electrical losses or contact or connecting points forming local elements are avoided as much as possible. The electrode **1** is inserted in the decomposition chamber **7** of the plant with its supporting structure so as to be insulated in relation to the mercury filling of this chamber, as will be seen from Fig. 2. The chamber in which the amalgam is formed is shown at **8**. The mercury is conveyed through the two chambers **7** and **8** in a cycle, e.g. by means of an oscillating pump **9**.

The electrode construction as per Fig. 1 is held in position for instance by attachments on the partition walls **10** and **11** so as to be fixed at minimum distance from the surface of the amalgam electrode **12**. In both chambers **7** and **8** contact plates **13** and **14** are arranged on the bottom through which plates a safe electric connection of the mercury electrodes of the two chambers **7** and **8** is ensured. **15** is the graphite electrode of the amalgam formation chamber **8**.

The electrochemical manner of operation of the arrangement as per Fig. 2 will be seen from the diagram of connection of Fig. 3. The graphite electrode **15** of the amalgam formation chamber **8** is connected to the positive pole of a source of direct current. At the electrode **15** gaseous chlorine is developed. In the appertaining mercury counter electrode **16** there is formed sodium amalgam which is conveyed into the decomposition chamber **7** by the mercury circulation. In the chamber **7** the metallic sodium is dissolved again in the form of sodium ions, in accordance with the process of the generation of current at the negative pole of a galvanic cell. On the nickel electrode **1** opposed to the amalgam electrode **12** gaseous hydrogen is developed in accordance with the reduction process on the depolarizing cathode of a galvanic cell. The nickel electrode **1** is connected to the minus pole of the source of direct current, whereby the entire circuit of the arrangement is closed. From the diagram of Fig. 3 it will be seen that the galvanic cell of the electrolytic chamber sodium amalgam

$$\text{—NaOH—Ni/H}_2\text{—}$$

is connected in series with the external source of direct current of the arrangement. The sum of the voltages of the two sources of direct current is the voltage required in the amalgam formation chamber for the decomposition of the alkali-chloride. Hence the voltage of the external source of direct current according to the invention is reduced by the voltage of the electrolytic cell.

In the arrangement as per Figs. 4 and 5 the depolarizing electrode according to the invention is used in a vertical mercury cell. The electrode plates **18** are secured to the cover **17** of insulating material by contact bolts **19**. These electrode plates according to the invention have a highly porous enlarged surface that may be formed by layers of nickel powder sintered on carrier plates. It is also possible to arrange highly porous sheets or foils on both sides of the surfaces of the carrier discs, for instance by spot welding, or to use other suitable constructions. The carrier plates **18** are secured to the contact bolts **19** at such a distance from each other that the rotary amalgamated immersing discs **20** are permitted to rotate therebetween with minimum distance on both sides. For the rotation of the discs **20** between the discs **18** in parallel planes it may be advantageous to provide on the stationary discs **18** or their supporting structure guide rollers or the like trueing the disc surface. The electrochemical action is the same as in the embodiment as per Fig. 2. The enlargement of the effective surface of the depolarization electrode **18** is particularly effective owing to the small parallel distance between the surfaces of the negative anodes **20** and the depolarizing cathodes **18**.

In the arrangement as per Figs. 4 and 5 the voltage drop in the interior of the electrolyte between the electrodes **18** and **20** (current density multiplied by internal resistance) is reduced to a minimum, since the large parallel surfaces of the electrodes result in a reduction of the internal resistance. It will thus be understood that by utilizing the voltage of the decomposition element in accordance with the invention it has become possible to use the vertical mercury cell also as an electrolytic cell in the alkali-chloride electrolysis. Figs. 6, 7 and 8 show an embodiment illustrating the constructional combination of an electrolytic cell with vertically rotating electrodes in the form of circular discs with a primary cell of the vertical rotation type in a unit. Preferably all rotating electrodes of the primary and secondary cells have a common carrier and driving shaft and the casing of the multicell unit is subdivided transversely to the axis of rotation of the rotary electrode by a stationary partition wall, in such a way that a chamber which is insulated from the adjacent chamber is provided for each

cell in the common casing, the mercury being circulated through the chambers in known manner by circulating pipes or ducts which may also be formed by channels in the casing of the unit.

This construction has proved to be a very favorable mode of realizing the invention.

A special advantage of the constructional form of an amalgam decomposing plant according to the invention consists in the fact that the rotors of both cells can be operated by a common driving motor if they have a common carrier and driving shaft as hereinbefore described. In this manner switching means for the control and survey as well as constructional parts and mercury are saved. It may also be advantageous, however, depending on the conditions of operation, to associate a separate driving motor to each of the cells combined into a constructional unit, more particularly by a flange, to that outer end wall of the cell of the unit which defines the cell operated by the motor arranged on it.

The primary cell **21** and the secondary cell **22** are constructed in per se known manner with vertically rotating electrodes **23** and **24** in the form of circular discs, said two cells **21** and **22** forming a constructional unit together with a common casing which is subdivided by a stationary transverse partition wall **25** transversely to the axis of rotation of the rotary electrodes **23** and **24** into chambers **21** and **22** electrically insulated from each other. All the rotary electrodes of the cells **21** and **22** are spaced from each other on the common carrier and driving shaft **26** and this shaft is driven by an electromotor **27** which is common for both cells **21** and **22**, through a worm drive **28**. The stationary electrodes **29** and **30** of the two cells **21** and **22** are arranged on the cover **31** of the casing, if desired in groups. **32** and **33** are filling pieces by which the cell space is diminished in order to reduce the amount of mercury required for filling this space. In order to regulate the formation of amalgam in the primary cell **21** and the decomposition of amalgam in the secondary cell **22** the electrodes of these cells are subdivided in such a manner, electrically and spatially, that the terminals **34** and **35** of the secondary cell permit a connection and disconnection of the negative electrodes belonging to this terminal **35**. A corresponding electrical and possibly also spatial subdivision is also provided for the primary cell by arranging terminals **36** and **37**. It will be understood that it is also possible to provide the constructional arrangement of the electrodes supported by the cover **31** of the casing in such in such a manner that the stationary electrodes belonging to one of the terminals **34**, **35**, **36** or **37** are supported by partial covers.

The cyclic flow of the mercury between the two cells **21** and **22** will be seen from Fig. 7. A circulating pump **39** is arranged in a connection pipe **38**, while an additional per se known decomposer **41** is provided in a circulating pipe **40** for decomposition of possible residual quantities of potassium or sodium in the mercury flowing back from the secondary cell **22** into the primary cell **21**.

The arrangement according to the invention with vertically rotating electrodes in the form of circular discs can also be used in connection with the so-called horizontal trough cells if vertically rotating electrodes in the form of circular discs arranged on a carrier and driving shaft with their axis of rotation in the longitudinal direction of the troughs or transversely thereto are inserted in a decomposition cell (secondary cell) with horizontal decomposing trough, said circular disc electrodes rotating between stationary electrodes outside of the mercury filling of the cell and filling pieces, more particularly filling discs, formed into or inserted in the trough. The stationary electrode discs hereat are preferably formed by sintered metallic skeletons, for instance, by discs having sintered skeleton foils applied on both sides.

This construction can also be used in a favourable

manner for the conversion of existing electrolytic cells with horizontal decomposition trough into cells with vertically rotating electrodes in the form of circular discs.

It is preferred to combine several sets of electrodes consisting of rotary and stationary electrodes into a constructional unit and to arrange such constructional units in the trough of the cell so that they can be exchanged. To this end, the exchangeable constructional units, more particularly in case of the conversion of existing horizontal trough cells, may be designed in such a way that they are carried by the cover of the cell and are coupled with each other in a coaxial series arrangement for common drive, so as to be easily disconnectible from each other. The cover of the cell also may be subdivided in such a way that each partial cover carries only one of the constructional units according to the invention which can be inserted into the trough of the cell. The constructional units may be surounded by casings whose end walls are perforated for the passage of the mercury and the lye and the accumulation of hydrogen between the spaces of the group of constructional units which are arranged in series. The covers of these casings carry the stationary electrode discs with the appertaining electrical connections which are insulated in relation to the rest of the casing.

The units with vertically rotating electrodes which are to be built into a horizontal decomposition trough together with their casings or the like form inserts by which the inner space of the trough is made to conform tightly to the rotary electrodes, in order to avoid unnecessary space in the cell which would have to be filled up with mercury. To this end, parts of the trough are filled up entirely with filling pieces, where in the conversion of a horizontal decomposing trough into a trough with vertically rotating electrodes it is not necessary to use the entire length of the trough for the required decomposing capacity. The construction according to the invention permits to enlarge the active electrode surface in the secondary cell in relation to the active electrode surface in the primary cell because the entire space of the trough can be used for arranging the rotary electrodes so that it is possible to provide a series arrangement of a large number of rotary discs with stationary electrode discs associated thereto, whereby the current density on the decomposition electrode is greatly reduced in accordance with the invention.

Examples for the use of vertically rotating electrodes in a horizontal decomposition trough in accordance with the invention are illustrated in Figs. 9, 10, 11, 12 and 13.

Fig. 9 shows a known horizontal primary cell **42**, combined with a horizontal decomposition or electrolytic cell **43** (secondary cell). Inserted in the cell trough **46** which is closed with a gas-tight seal by covers **44** and **45** are constructional units **47** formed by vertically rotating circular disc electrodes **48** and stationary sintered skeleton disc electrodes **49**. The circular disc electrodes **48** are carried by a shaft **50** which is common for all rotary electrodes of a constructional unit and mounted in the end walls **51** and **52** of the casing enclosing the electrode set of one constructional unit. Inserted in the bottom **53** of the casing are filling pieces **54** projecting between the rotary electrode discs in the region of the mercury filling of the cell in order that the free space and so the amount of mercury required for the cell may be reduced to a minimum. The stationary electrode discs **49** are supported by the cover **55** of the casing so as to be interchangeable. Any desired number of constructional units **47** may be arranged axially behind each other in a cell trough. The constructional units are coupled with each other for common drive in per se known manner and all rotary electrodes provided in a cell trough **46** are driven by a common motor **56** advantageously through a worm drive. The constructional units with their casings are carried by the trough covers **44** and **45**.

The end walls **51** and **52** of the constructional units

47 are provided with perforations 57 and 58 in the region of the mercury filling of the cell and in the region of the hydrogen accumulating space formed by the cell, in order that the mercury may be permitted to circulate through the trough 46 of the electrolytic cell and of the cell 42 for the formation of amalgam, under action of the pump 59. The perforations 58 serve to form a common gas accumulating chamber for all constructional units 47 in the horizontal cell 46 fitted therewith. In per se known manner the trough covers 44 and 45 are electrically insulated with respect to the rest of the casing and these covers carry the means for the connection of the stationary electrode discs 49.

Fig. 12 shows the circulation of the mercury in the constructional units 47 which are arranged in series and the connections of the circulation pipe 60, 61 leading to the primary cell 42 are also indicated.

It will be seen from Fig. 13 that the rectangular cross section of the hollow trough 46 by arrangement of inserts 62 and 63 is made to conform as much as possible to the circular profile of the rotary electrode discs 48. Of course, in case of a new design of horizontal trough cells with vertically rotating packs of electrodes the basic cross section of the trough 46 corresponds to the shape of the rotary electrodes.

The electrodes which are preferably used according to the invention, having roughened surfaces or being sintered so as to be porous, more particularly at their surface, have the great advantage that the amalgam or mercury has a high surface adhesion on such surfaces and these electrodes therefore are also suitable for realizing a design and arrangement of the electrodes in the electrolytic cell which hitherto was not technically possible, the amalgamated mercury trickling down over vertical metallically conductive surfaces, because the rough surface of the electrodes in case of a corresponding shape of the same forms a multitude of fine grooves disposed closely beside each other and ensuring a uniform distribution of the liquid metal as the same trickles down over the surface of the electrodes. The electrodes may also be formed by a fabric or mesh screen, perforated metal sheets or the like coated on one or both sides with a highly porous sintered metal powder layer and combined with each other. With such electrodes the trickling surface is made as uneven as possible in order to ensure that the trickling metal forms a uniform layer over the entire outer surface of the electrode, avoiding exposed spots. To this end, the sintered layer should envelop the support or insert material completely, also at the cut surfaces thereof. The electrodes according to the invention may also be shaped in the form of pockets, in such a way that the mercury enriched with amalgam flows into the electrode pocket which is as flat as possible and flows off through pores, holes, slots or the like in the pockets of the walls, over the outer electrode surface, so as to be distributed accordingly.

Owing to the fact that in the process of decomposition of amalgam according to the invention the decomposition is effected with the aid of an electrode which is not electrically short-circuited with the amalgam electrode, the danger exists, that in case the voltage connected to the primary cell falls below the decomposition voltage of alkali-chloride, the mercury which is rich in amalgam flows back into the primary cell without being decomposed, whereby considerable disturbances can be caused.

A further object of the invention is to eliminate such deleterious effects in case of a voltage drop. This is attained in such a way that a voltage controlled relay or the like is inserted in the decomposition circuit of the secondary cell which relay in case of a dropping of the voltage below the decomposition voltage of the alkali-chloride short-circuits the amalgam electrode with the electrode developing hydrogen. In case of a deleterious voltage drop in the secondary cell the decomposition of the amalgam goes on according to the principle of the per se known self-decomposing cells until the amalgam still present in the circulating mercury is completely decomposed.

The measure according to the invention requires a special manipulation for the starting of the orderly decomposing process after the cessation of the voltage drop which is to be regarded as deleterious for the operation. For the beginning of the electrolysis the short circuit between the amalgam electrode and the electrode developing hydrogen is opened by the said relay in dependence upon the voltage. In order that the secondary cell comes into effect only when the mercury passing through this cell has the sodium contents required for orderly operation, the circuit of the secondary cell is disconnected up to this point of time simultaneously with the cessation of the short-circuit. The time required for starting the electrolysis can be calculated from the current intensity and the amount of mercury which is circulating. A time relay may be provided for connecting again the circuit of the secondary cell, whereby the normal course of the electrolysis is automatically started again without particular attendance.

The circuit arrangement according to the invention is exemplified in Fig. 14. The primary cell is shown at 64 and the secondary cell is shown at 65. As the voltage of the external source of current 67 falls, the amalgam electrode 68 is short-circuited with the electrode 69, developing hydrogen, through a relay 66. As the voltage of the external source of current 67 again rises above the decomposition voltage, this short circuit is opened again. In order to avoid that after an interruption of operation by sudden voltage drop or by an intended disconnection of the plant the decomposition in the secondary cell begins as the plant is again taken into operation, before a sufficient amount of amalgam is present in the mercury circulation system, there is arranged a time-delay relay 70 by which the secondary cell is connected to the external source of current 67 only when an amount of amalgam sufficient for the normal decomposition process is present in the secondary cell owing to the mercury circulation.

In the alkali-chloride electrolysis according to the invention gaseous chlorine is formed in the primary cell from sodium chloride on a graphite anode and sodium amalgam is produced on a mercury cathode. In the secondary cell the sodium amalgam is decomposed with formation of NaOH and hydrogen. The decomposition energy can be utilized electrolytically if the secondary cell is connected in series with the external source of direct current. The voltage connected to the primary cell in this case is increased by the voltage supplied from the secondary cell. The current intensities in the primary cell and in the secondary cell are equal in case of series connection and hence in the unit of time the same amount of amalgam is produced which is decomposed in the secondary cell. If, as it is the case in practice, a part of the amalgam formed in the primary cell owing to auxiliary reactions is again decomposed in the primary cell, an impoverishment of amalgam occurs in the secondary cell in the course of the electrolysis, which may lead to disturbances in the course of the electrolysis. The current intensities in the primary cell and in the secondary cell therefore must not be equal but must be adapted to the yield of current in the two cells. We have found that the process advantageously should be carried through in such a way that the current intensity in the primary cell is higher than that in the secondary cell, i.e. by about 5 to 10 percent.

According to a further feature of the invention, for harmonizing the current intensities in the primary and secondary cells with the current yields in these cells, i.e. for compensating the losses by self-decomposition or the like in the primary cell, an additional electrode is arranged in this cell which electrode is not connected through the decomposing cell to the external source of

direct current supplying the electrolyzing current. By arranging these subdivided electrodes in the primary cell and using the said circuit arrangement for the auxiliary electrode it is possible to adapt the current intensities in the primary and secondary cells to the yields of current. If the yield of current in the primary cell would change, this in case of a constant ratio of the areas of the two electrodes would lead to disturbances in the course of time. This can be taken care of by changing the ratio of the surface areas of the two electrodes of the primary cell or by possible arrangement of an adjustable resistance 75 in the circuit of the auxiliary electrode of the primary cell. For carrying out the electrolysis continuously it is advantageous to adjust the ratio of the surface areas of the two electrodes in the primary cell in such a way that the current intensity in the secondary cell is somewhat lower than that which would correspond to the maximum yield of current. For instance, a yield of 90 percent instead of 95 percent of the current intensity will be provided in the primary cell. The mercury leaving the secondary cell thereby has still a small residual contents of sodium corresponding to the smaller current intensity in the secondary cell. In order to avoid summation of these residual quantities of sodium in case of a continuous circulation of the mercury, according to a further feature of the invention an additional decomposer, more particularly of the type of the known graphite decomposers is arranged in the mercury circulating system between the secondary cell and the primary cell, for decomposing the residual amalgam, so that the mercury flowing back into the primary cell is perfectly free from amalgam. In such an additional decomposer acting as a buffer, fluctuations of the yield of current are simultaneously compensated automatically. Preferably the additional decomposer in per se known manner is constructed as a so-called wash tower or spray column, in such a way that the flow of mercury on its passage through this tower is automatically interrupted and the electrical insulation of the mercury between the primary and secondary cells required for carrying out the method according to the invention is produced.

The circuit diagram and arrangement to be used for this purpose is exemplified in Fig. 15. The graphite anodes 71 and 72 are subdivided into a portion 71 of a large surface area and a portion 72 of a smaller surface area. The two electrodes are electrically insulated from each other. The electrode 71 is connected with a nickel electrode 73 of the secondary cell. The subelectrode 72 is directly connected to the positive pole of the external source of current 74. The ratio of the current intensities in the primary and secondary cells are determined by the ratio of the surface areas of the electrodes 71 and 72. The current intensity in this circuit may also be variable by adjustment of a resistance in the circuit of the auxiliary electrode 72. For the manner of operation of the adjustment hereinbefore described it is necessary that the mercury in the primary cell is electrically separated from the amalgam in the secondary cell. This can be achieved by the provision of per se known circulating pumps or the like interrupting the flow of mercury. The ratio of the surface areas of the electrodes 71 and 72 is determined by certain rules which have been found out experimentally or by calculations. Preferably the ratio of the actively acting surface areas of the electrodes of the primary cell will be selected in such a way that the current intensity of the primary cell is about 5 to 10 percent higher than that in the secondary cell so as to obtain an adaptation to the yield of current in the two cells.

While the invention has been described in detail with respect to certain now preferred examples and embodiments of the invention it will be understood by those skilled in the art after understanding the invention that various changes and modifications may be made without departing from the spirit and scope of the invention and it is intended, therefore, to cover all such changes and modifications in the appended claims.

We claim:

1. In an alkali-metal-chloride electrolysis process wherein an alkali metal chloride solution is electrolyzed in a primary cell having a graphite anode and a mercury cathode to form chlorine gas and an alkali metal amalgam, said amalgam being conducted to a secondary amalgam decomposition cell containing a hydroxide electrolyte and having a depolarization electrode from which hydrogen is liberated, said amalgam serving in said decomposition cell as an amalgam electrode at which the amalgam is decomposed to form alkali-metal ions and alkali-metal-free mercury, said alkali-metal-free mercury being returned to said primary cell for reuse as the mercury cathode thereof; the method of causing said decomposition cell to function as a voltage source to produce electrical energy to assist in the electrolysis of the solution in the primary cell, which comprises the steps of connecting the negative terminal of a direct-current voltage source to the depolarization electrode of said decomposition cell, connecting the positive terminal of said direct-current voltage source to the graphite anode of said primary cell, electrically connecting the amalgam electrode of said decomposition cell to the mercury cathode of said primary cell so that said decomposition cell will be connected as a current-supplying galvanic cell in series with said primary cell and said direct-current voltage source, and using as the depolarization electrode of said decomposition cell an electrode having a porous sintered electrically-conductive surface, said sintered surface consisting of at least one substance selected from the group consisting of nickel powder and iron powder.

2. A cell for the electric utilization of the decomposition energy of amalgams comprising a cell vessel for containing a hydroxide electrolyte, an amalgam electrode in said cell vessel, a depolarization electrode in said cell vessel opposite said amalgam electrode, said depolarization electrode having a potential more noble than the potential of the amalgam electrode during the amalgam decomposition, said depolarization electrode also having a porous sintered electrically-conductive surface, said sintered surface consisting of at least one substance selected from the group consisting of nickel powder and iron powder.

3. A cell as defined in claim 2 wherein said depolarization electrode consists of a plurality of spaced planar elements arranged normal to the active face of the amalgam electrode.

4. A cell as defined in claim 3, wherein each of said planar elements includes a thin metal foil, and further wherein said sintered surface is constituted by porous sintered layers on both sides of each of said thin metal foils.

5. A cell as defined in claim 3, wherein said planar elements are connected in the form of a continuous serpentine.

6. A cell as defined in claim 2 wherein said amalgam electrode includes a plurality of rotatably mounted metal disks covered with amalgam by immersion of their lower parts into the amalgam, and further wherein said depolarization electrode includes a plurality of stationary elements, said stationary elements being on each side of and spaced out of contact with said rotating metal disks.

7. A cell as defined in claim 6, wherein each of said depolarization electrode elements comprises a carrier plate having porous foils contiguously arranged on both sides of said plate.

8. Apparatus for electrolyzing an alkali-metal chloride solution comprising a primary cell including a primary cell vessel for containing said solution, and a graphite anode and a mercury cathode in said primary cell vessel, said solution being electrolyzed in said pri-

mary cell to form chlorine gas and an alkali-metal amalgam; a secondary amalgam decomposition cell including a cell vessel for containing a hydroxide electrolyte, and a depolarization electrode in said decomposition cell vessel; means feeding said amalgam from said primary cell vessel to said decomposition cell vessel, said amalgam constituting the amalgam electrode of said decomposition cell, said amalgam being decomposed in said decomposition cell to form alkali-metal ions and alkali-metal free mercury, said depolarization electrode having a porous sintered electrically-conductive surface consisting of at least one substance selected from the group consisting of nickel powder and iron powder; a direct-current voltage source; circuit means connecting the secondary amalgam decomposition cell as a current-supplying galvanic cell in series with said primary cell and said direct-current voltage source, said circuit means including means electrically connecting the graphite anode to the positive lead of said direct-current voltage source, means electrically connecting said depolarizing electrode to the negative lead of said direct-current voltage source, and means electrically connecting said amalgam electrode with said mercury cathode; and means for recycling the alkali-metal-free mercury from said decomposition cell to said primary cell for use as the cathode thereof.

9. Apparatus as defined in claim 8 wherein said mercury electrode of the primary cell comprises a plurality of vertically-arranged rotatably-mounted metal disks covered with mercury by immersion of their lower parts into the mercury, each of said disks being intermediate two of a plurality of stationary spaced parallel vertical graphite members forming the graphite anode of said primary cell, and further wherein said amalgam electrode of the secondary cell comprises a plurality of vertically-arranged rotatably-mounted metal disks covered with amalgam by immersion of their lower parts into the amalgam, each of said disks being intermediate two of a plurality of stationary spaced parallel vertical elements forming said depolarization electrode, the axes of rotation of said electrodes being colinear, and further including common drive shaft means for rotatably driving said electrodes.

10. Apparatus as defined in claim 8, wherein said secondary cell vessel comprises a horizontal trough, and further wherein said depolarization electrode comprises a plurality of stationary spaced parallel vertical members and said amalgam electrode comprises a plurality of vertically-arranged rotatably-mounted disks covered with mercury by immersion of their lower parts into the amalgam, each of said disks being intermediate two of said stationary depolarization members.

11. Apparatus as defined in claim 10 wherein a plurality of sets of said depolarization electrodes and said amalgam electrodes are interchangeably positioned in said horizontal trough.

12. Apparatus as defined in claim 8 including a graphite anode in said primary cell consisting of two separate anode parts electrically insulated from each other, one of said anode parts being smaller than the other and serving as an auxiliary anode for regulating the current efficiencies, said smaller anode part being connected directly with the positive lead of the direct current voltage source, said positive lead of the direct current voltage source being also connected directly with the amalgam electrode of the secondary amalgam decomposition cell, and the larger part of said two anode parts serving for conducting the main part of the current necessary for the electrolysis of the alkali chloride solution in the primary cell vessel and being connected directly with the depolarization electrode of said secondary cell.

13. Apparatus as defined in claim 12 and further including a variable resistor connected in series with said auxiliary anode.

14. Apparatus as defined in claim 8 and further including voltage-controlled relay means in the electrical circuit of the decomposition cell, said relay means being effective to short circuit the amalgam electrode with the depolarization electrode when the voltage of the direct current source drops below the decomposition voltage of the alkali metal chloride solution.

15. Apparatus as defined in claim 14 and further wherein said voltage-controlled relay means is effective to break the short circuit upon the resumption of electrolysis when the voltage rises again above the desired level, and delay means for preventing operation of the secondary amalgam decomposition cell until the mercury passing through it again exhibits the desired amalgam content.

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