June 1, 1971 HIROSHI SHIBATA ET AL 3,582,524

MERCURY-PROCESS ELECTROLYTIC APPARATUS

Filed June 28, 1968 2 Sheets-Sheet 1

FIG. 1

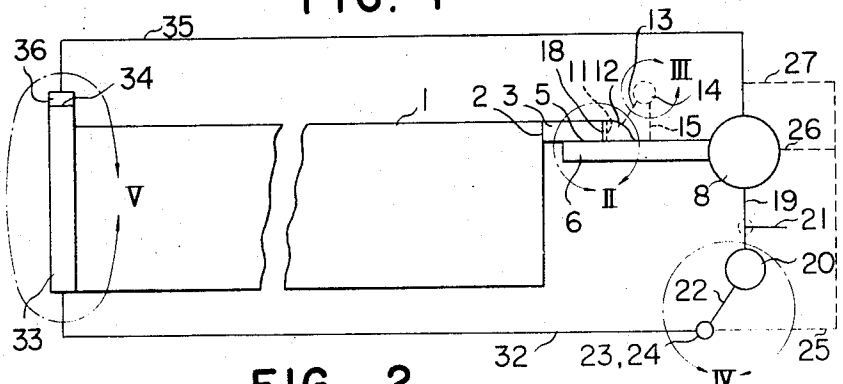


FIG. 2

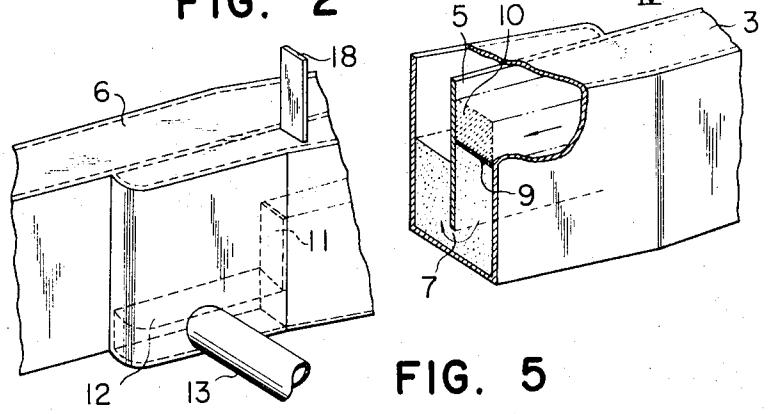
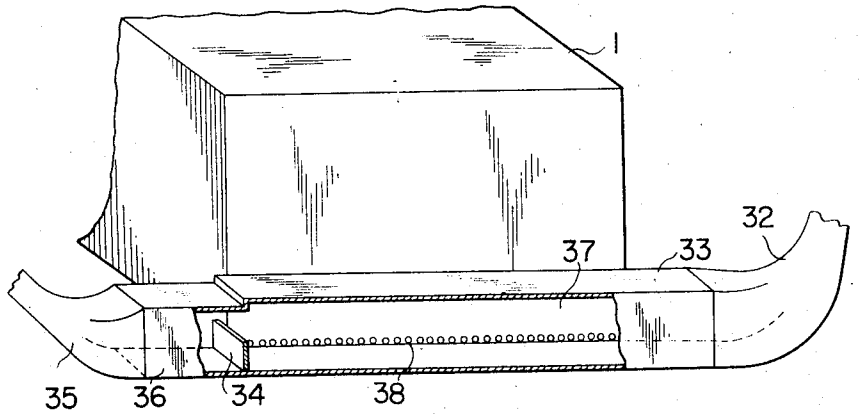


FIG. 5



June 1, 1971 HIROSHI SHIBATA ET AL 3,582,524

MERCURY-PROCESS ELECTROLYTIC APPARATUS

Filed June 28, 1968 2 Sheets-Sheet 2

FIG.3

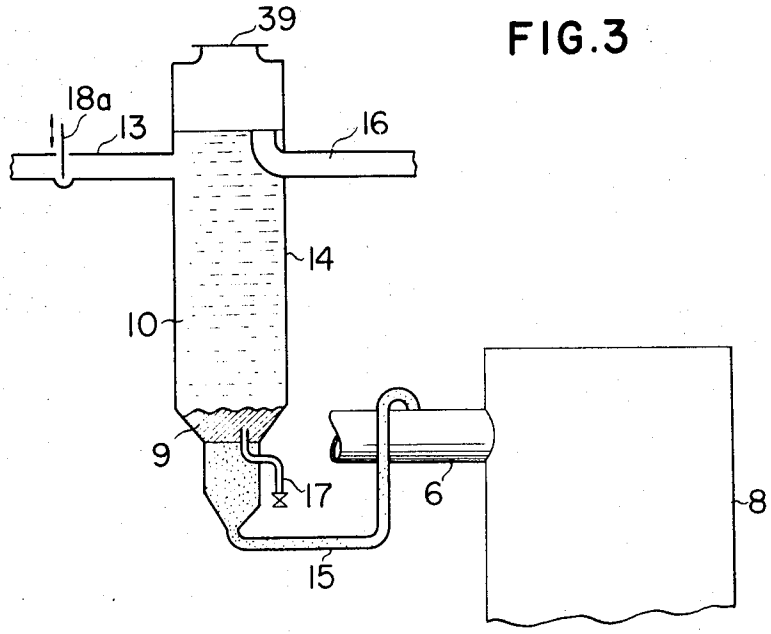
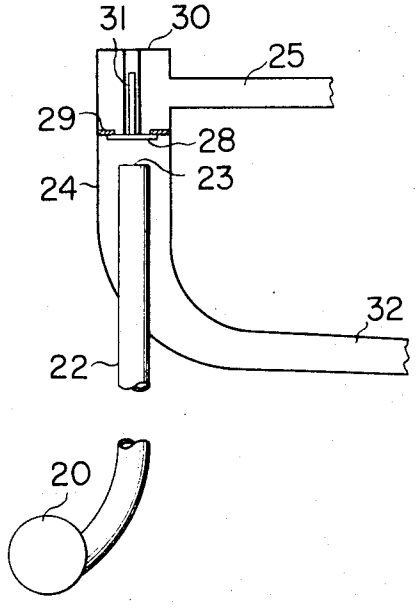


FIG.4



United States Patent Office 3,582,524 Patented June 1, 1971

3,582,524

MERCURY-PROCESS ELECTROLYTIC APPARATUS

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Int. Cl. C22d 1/04
U.S. Cl. 204—220 4 Claims

ABSTRACT OF THE DISCLOSURE

The main mercury circulation system through an electrolytic cell, a denuding device, and a mercury pump in a mercury-process electrolytic apparatus is fully sealed and isolated from the atmosphere during operation and is provided with a separation device outside of the system for removing contaminants from the mercury amalgam conducted from the electrolytic cell to the denuding device, a device for preventing backflow of mercury when the mercury pump stops, and a bypass device for circulating contaminants within denuded mercury, together with a part of this mercury and wash water, back to the denuding tower.

BACKGROUND OF THE INVENTION

This invention relates generally to the field of mercury-process electrolysis and apparatuses therefor and more particularly to a new technique whereby the main mercury circulation system comprising principally an electrolytic cell, a denuding device, and a mercury pump in a mercury-process electrolytic apparatus is operated in a state of isolation from the atmosphere.

In mercury-process electrolysis, in general, mercury which has flowed through an electrolytic cell (known also as a mercurycathode cell) and become an amalgam is separated from the electrolyte and sent to a denuding tower, where the mercury is denuded by denuding water and thereby recovered. The mercury thus recovered is then first raised by a mercury pump to a hydrostatic level higher than the mercury surface level within the electrolytic cell and, from this higher level, flows into the electrolytic cell.

During the electrolysis in the electrolytic cell, impurities such as magnesium and calcium salts and iron within the electrolyte intermix with graphite particles broken off from the graphite anode, mercury amalgam, and the electrolyte to form a butter-like emulsion (generally called "mercury butter"). This emulsion, free particles broken off from the graphite anode (hereinafter referred to as graphite particles), and other contaminants are arrested and caused to accumulate in a stagnant state by a baffie placed at the downstream end of the electrolytic cell within the cell or in a passageway outside of the cell. From time to time the apparatus enclosure housing the baffie part is opened, and the contaminants thus collected are removed by scooping.

At such parts of the apparatus where contaminants are accumulated in a static state, electrolytic brine liquor in which chlorine is dissolved is present in the upper part of the process liquids. Consequently, when the enclosure of such parts is opened, chlorine is given off and not only is harmful to the health of the operator engaged in the work of removing the contaminants but also leaks in large quantity into the electrolysis room. In brine electrolysis as practiced in recent years, moreover, very high current desities are employed in order to increase the production efficiency per unit electrolysis area. As a result,

the rates of formation of substances such as mercury butter are also high, and in many instances an electrolytic cell requires several removals per day of contaminants by scooping.

The mercury which has been discharged from the denuding tower is first pumped by the mercury pump to a high level and then flows to the electrolytic tank as mentioned hereinbefore. However, if the operation is carried out with the flow path connecting the mercury pump and the electrolytic cell in a fully enclosed and sealed state, and if the mercury pump stops because of an abnormal occurrence such as a power failure, the mercury in the piping on the pump delivery side will fall back under its own heavy weight to the pump and create a vacuum within the piping. Furthermore, this vacuum will cause not only the mercury in the flow path to the electrolytic cell but also the amalgam and electrolyte within the electrolytic cell to undergo a reverse flow or backflow toward and into the pump delivery circuit. For this reason, the upper end of the riser pipeline on the delivery side of the mercury pump is ordinarily opened to the atmosphere in a flow circuit of this character.

Exposure of the mercury to air in this manner, however, causes oxidation of the mercury surface which gives rise to a problem since oxidised mercury readily forms mercury butter in the electrolytic cell.

In addition, the mercury which is recovered and is separated from caustic soda in the denuding tower mixes with graphite particles arising from the disintegration of the denuding graphite granules in the tower and with caustic soda soltuion to form an emulsion. Furthermore, the vigorous agitating action of the mercury pump causes the mercury to form, together with wash water, an additional large quantity of mercury emulsion within the pump. These contaminants, also, have heretofore been removed by static accumulation and scooping at a point upstream from the electrolytic cell.

SUMMARY OF THE INVENTION

It is a first object of the present invention to provide a mercury-process system of the type referred to above wherein the main mercury flow path from the electrolytic cell to the denuding tower is constantly and totally sealed during operation thereby to prevent leakage of chlorine.

A second object of the invention is to provide a mercury-process system wherein the closed circuit for mercury circulation is totally sealed constantly during operation thereby to prevent infiltration of air into this circuit.

A third object of the invention is to provide a mercury-process system wherein contaminants such as mercury butter formed in the electrolytic cell and graphite particles are separated from the mainstream mercury into a bypath outside of the main mercury circuit together with a small quantity of mercury separating from the mainstream mercury, and the removal of these contaminants is carried out outside of the main mercury circuit thereby to reduce the frequency of removal of contaminants, to simplify the operational procedures, and, at the same time, to improve the work environment of the electrolysis operation.

A fourth object of the invention is to provide, in a mercury-process system, means for causing foreign matter such as mercury emulsion formed in the denuding tower and the mercury pump, together with a small quantity of mercury, to recirculate to the denuding tower thereby to eliminate the work of removing mercury emulsion from the flow circuit upstream from the electrolytic cell.

A fifth object of the invention is to provide, in a mercury-process system, a closed circuit for mercury circulation which is fully sealed during operation and to provide means to prevent backflow of amalgam and

electrolyte within the electrolytic cell into the mercury pump pathe which backflow would otherwise occur when the mercury pump is stopped.

A sixth object of the invention is to provide, in conjunction with the achievement of the above fifth object, improvement in the mercury flow path from the mercury pump to the electrolytic cell.

A seventh object of the invention is to provide, in conjunction with the achievement of the above third and fourth objects, improvement in the separation of mercury.

According to the present invention, briefly summarized, there is provided a mercury-process apparatus of the type referred to hereinabove in which a passageway fully sealed from the outside atmosphere is used for conducting mercury amalgam from the electorlytic cell to the denuding tower, and a separation device for removing contaminants from the mercury amalgam is disposed outside of this passageway.

According to the present invention, in another aspect thereof, there is provided a mercury-process apparatus of the above stated character in which the main mercury circulation system is fully sealed, and there are provided in combination therewith the above mentioned separation device, a device for preventing backflow of mercury when the mercury pump stops, and a circulation device for causing contaminants within denuded mercury to circulate, together with a part of the mercury and wash water, back to the denuding tower.

The nature, principles, details, and utility of the invention will be more clearly apparent from the following detailed descripion with respect to a preferred embodiment of the invention, when read in conjunction with the accompanying drawings, in which like parts are designated by like reference numerals.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

FIG. 1 is a flow chart indicating the essential organisation of one example of a mercury-process system constituting a preferred embodiment of the invention;

FIG. 2 is a fragmentary perspective view, with parts cut away and with some parts in section, showing the details of the part designated by enclosure II in FIG. 1;

FIG. 3 is an elevational view, in vertical section, of the part designated by enclosure III of FIG. 1;

FIG. 4 is an elevational view, in vertical section, of the part designated by enclosure IV of FIG. 1; and

FIG. 5 is a fragmentary perspective view, with parts cutaway and with parts in section, showing the part designated by enclosure V in FIG. 1.

DETAILED DESCRIPTION

Refering first to FIG. 1, mercury which has flowed the electrolytic cell **1** and become an amalgam flows under and past a gas partition at the downstream end **2** of the cell, together with a portion of dilute brine and foreign matter or contaminants, and is discharged out of the cell through a passageway **3**.

The mercury in the passageway **3** is separated out from the other accompanying matter by a method wherein the mercury or mercury amalgam, contaminants, and liquid are caused to flow together through a first duct means having a length substantially greater than the width thereof, the mercury or mercury amalgam being caused to pass under and past a baffle into a further duct means which is parallel and in side-by-side disposition with the first duct means, the baffle forming a common, partial side wall between the ducts and having an opening thereunder and below the upper surface of the mercury or mercury amalgam so as to permit passage only of the mercury or mercury amalgam through the opening and blocking passage of the contaminants and the liquid. See our copending application No. 691,413 filed on Dec. 18, 1967. More specifically, most of the merucy in passageway **3**, as shown in FIG. 2, flows into a passageway **6**, which is parallel and contiguous to the passageway **3**

with a common side wall **5** disposed therebetween, through a vertically narrow gap **7** provided below the lower edge of the side wall **5** and is sent through the passageway **6** to the denuding tower **8**.

On the other hand, contaminants **9**, together with a small quantity of mercury and dilute brine **10**, overflow over an overflow weir **11** provided at the downstream end of the passageway **3** and into an overflow mercury sump **12**. Most of the dilute brine discharged from the electrolytic cell is discharged through a separate outlet (not shown).

By this organisation and functions of parts, the brine and contaminants flowing along the passageway **3** ride on and are swept along by the surface flow produced by the small quantity of mercury overflowing over the weir **11**, all of this brine and contaminants thereby flowing into the mercury sump **12**, Accordingly, there is no possibility of contamins and brine being mixed with the mainstream mercury entering the passageway **6**. Therefore, the electorlysis operation can be carried out with the electrolytic cell **1**, passageway **3**, and pasageway **6** in a fully sealed state.

Since the mercury sump **12** is outside of the mercury mainstream, and there is no possibility, when contaminants such as mercury butter are accumulated therein of these contaminants flowing into the passageway **6** to the denuding tower **8**, it is possible to accumulate these contaminants in the sump **12** over a long period of time and to remove these contaminants thus accumulated by scooping through a small, closable scooping aperture provided above this sump.

By making the surface area of the mercury sump **12** and the scooping aperture small, the quantity of chlorine gas given off and, therefore, the quantity of chlorine leaking out when the aperture is opened for scooping can be reduced to a very small quantity. An alternative and more effective method, however, is to provide a gate device as, for example, a sluice gate **18** which can be opened and closed in the vertical direction, at a point upstream from the weir **11** and to shut off the brine flow during the scooping work. Furthermore, depending on the circumstances, it is possible to fix the height of the sluice gate **18** and permit brine to flow continually therepast at a low flow rate thereby shutting off and isolating the upper space of the sum **12** from the upper space of the passageway **3**.

The small quantity of mercury which flows into the mercury sump **12**, together with the contaminants is drained out of the lower part of the sump **12** in a manner to preserve the mercury hydrostatic head at a constant value and may be returned to the passageway **6** to the denuding tower without any possibility of contaminants or brine accompanying the mercury since the mercury flowrate is very low.

Depending on the circumstances, however, the mercury thus drained out and brine are conducted by a passageway such as passageway **13** into a contaminant separation vessel **14** as shown in FIG. 3, where the mercury is separated out and sent through a path **15** to the denuding tower **8**, while the diluted brine is recirculated through a pipeline **16** to the brine dissolving process (not shown). Only the contamiants in a static state at an intermediate position are removed from time to time by scooping through a scooping aperture **39** or are drained out through a discharge pipe **17**.

In this case, the chlorine can be reduced to facilitate the operator's work by a suitable method such as: providing a sluice gate **18***a* in the passageway **13**, closing this sluice gate at the time of contaminant removal to shut off the brine, and diluting with water the chlorine in the small quantity of brine remaining in the separation vessel **14**; drawing away the chlorine gas by means of a suction fan; or adding a chlorine remover such as sodium thiosulphate.

By the above described operation technique, there is no necessity whatsoever of opening the main flow path from

the electrolytic cell **1** to the denuding tower **8**, even during a long period of electrolysis operation. Furthermore, the frequency with which the mercury butter and other contaminants must be removed in the bypath is substantially decreased, and, moreover, it is possible also to prevent chlorine gas from being given off during this contaminant removal. Accordingly, the work environment can be thoroughly improved, and, in addition, erosion of apparatus parts due to chlorine gas can be eliminated or greatly reduced.

In addition, it is desirable that the entire process circulation path from the outlet of the denuding tower **8** to the electrolytic cell **1** be completely sealed. That is, in this circulation path, the mercury which has been sent from the denuding tower **8**, through a passageway **19**, and to the mercury pump **20** is ordinarily supplied with water added thereto through an inlet **21** and is thereby washed in the pump **20** and relates piping. The downstream end **23** of the riser pipe **22** on the delivery side of the pump **20** is ordinarily open to the atmosphere as mentioned hereinbefore.

In the electrolysis apparatus of the invention, this part of the circulation path is sealed and isolated from the atmosphere but connected directly or indirectly to the denuding tower **8**. More specifically, referring to FIGS. 1 and 4, the mercury which overflows from the end **23** of the riser pipe **22** flows into the space between the riser pipe **22** and an outer pipe **24**, through the lower part of this pipe **24** and a pipeline **32**, to the electrolytic cell **1**.

The upper end of the outer pipe **24** is closed and communicates through a side **25** directly (through the path of pipes **25** and **26**) or indirectly (through the path of pipes **25** and **27**, for example) with the denuding tower **8**. In some cases, an automatic check valve **28** may be provided above the end **23** of the riser pipe **22** for the purpose of preventing mercury and wash water which have been caused by the delivery pressure of the pump **20** to rise rapidly up through the riser pipe **22** from flowing under their kinetic energy through a path of the side pipe **25** and into the denuding tower **8**.

While the pump **20** is operating, the valve **28** is pressed upward in closed position by the fluid dynamic pressure of the mercury thereby to shut off the path of the side pipe **25**. When the pump **20** stops, the valve **28** is caused to drop by its own weight and a vacuum which is produced in the riser pipe **22** thereby to close the upper end **23** of the riser pipe and prevent back flow of mercury downstream from pipe **24** due to the vacuum.

While the valve **28** may be of any design suitable for its function, the valve **28** in the illustrated example comprises a valve body **28**, a valve seat **29** supported by pipe **24** for closure seating of the valve body **28**, and guide means comprising a stationary guide tube **31** and a rod **30** fixed to and supporting the valve body **28** and slidably disposed within the guide tube **31**.

By the above described organisation, the mercury is prevented from contacting the air of the outside atmosphere. Moreover, even if the mercury pump **20** stops suddenly because of an occurrence such as a malfunction in the electrical system, and a vacuum is created within the pipe **22**, the only result is that the mercury or water and other substances in the denuding tower **8** or passageways communicating therewith (the principal substance flowing through a return pipe **35**, described hereinafter, being water which has washed supply mercury for the electrolytic cell) merely undergo backflow, and there is no backflow of the analgam and electrolyte within the electrolytic cell to the supply mercury passageway and the mercury pump **20**.

While, in this example of the invention, the upper part of the outer pipe **24** is connected to the denuding tower **8**, this upper part can be connected to a water supply pipe, in some cases, thereby to cause water to flow into the riser pipe **23** when the pump stops.

Under normal operation, the mercury in the pipe **24** flows through a pipe **32** and enters a mercury separation passageway **33**, where most of the mercury is separated out to flow into the electrolytic cell **1**. The remainder of the mercury, together with mercury butter, foreign matter such as graphite particles, and wash water existing thereabove, flows over an overflow weir **34** at the downstream end of the passageway **33** as shown in detail in FIG. 5 and, entering an inlet **36** of the aforementioned return pipe **35**, flows through the pipe **35** to the denuding tower **8**.

The principle of the mercury separation in the mercury separation passageway **33** as shown in detail in FIG. 5 is the same as that of the mercury separation indicated in FIG. 2. That is, the mercury separation passageway **33** may be considered to correspond to the mercury outlet passageway **3** shown in FIG. 2, and the upstream end of the electrolytic cell **1** may be considered to correspond to the separated mercury passageway **6**. Furthermore, the weir **34** and inlet **36** may be considered to be analogous respectively to the weir **11** and sump **12** illustrated in FIG. 2.

These two mercury separation operations are different, however, in that whereas the direction of mercury flow in the passageway **6** is parallel to that in the passageway **3** in the separation device shown in FIG. 2, the directions of mercury flow in the passageway **33** and electrolytic cell **1** in the separation device shown in FIG. 5 are perpendicular. Consequently, if the mercury inlet at the lower part of the boundary side wall **37** between the passageway **33** and the cell **1** were to be in the form of a narrow slot as in the separation device shown in FIG. 2, the mercury flowing through the slot into the cell would have a momentum of flow in the same direction as the flow in the passageway **33**. Accordingly, it is preferable to make this mercury inlet into the cell in the form of a plurality of small holes **38** as shown in FIG. 5.

The wash water sent through the pipe **35** to the denuding tower **8** is used again as denuding water and, in the example illustrated in FIG. 1, is conducted by the pipe **35** directly to the denuding tower **8**. Alternatively, however, the downstream end of the pipe **35** can be connected to a part of the passageway **6** for amalgam flowing to the denuding tower **8** thereby to send the wash water together with the amalgam to the denuding tower.

Heretofore, it has been the practice to provide a baffle at the upstream end or the downstream end of a passageway such as the passageway **33** to collect contaminants in a stagnant state and to scoop out from time to time the contaminants thus collected. In the system according to the invention, however, since there are no points at which contaminants can accumulate in a static state, the possibility of contaminants and alkaline wash water in stagnant state flowing into the electrolytic cell is eliminated, and, moreover, the troublesome and unhealthy work of scooping out contaminants becomes unnecessary.

Furthermore, since the fully enclosed system of the invention is not opened during operation for removal of contaminants, undesirable occurrences due to infiltration of air such as lowering of the purity of the mercury sent to the denuding tower and oxidation of the mercury are eliminated.

The constituents of the mercury emulsion formed in parts of the system such as the denuding tower and the mercury pump, differing from those of the mercury butter formed within the electrolytic cell, are restored with relative case to their original states prior to emulsification. We have found that, therefore, although this mercury emulsion is circulated to the denuding tower in the system of the invention, there is no cumulative increase in the mercury emulsion.

Furthermore, since most of the denuding graphite particles are removed together with caustic soda and separated by means such as a filter, there is no possibility of accumulation of these particles even when the separation of the particles accompanying the circulating mercury is stopped.

In the case wherein the mercury leaving the denuding tower is first led into a mercury sump and then charged into the mercury pump, the upper part of this mercury may be sealed with water, but an even more effective measure is to provide means for communicating the space above the mercury sump to the interior of the denuding tower.

It should be understood, of course, that the foregoing disclosure relates to only a preferred embodiment of the invention and that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purposes of the disclosure, which do not constitute departures from the spirit and scope of the invention as set forth in the appended claims.

What we claim is:

1. A fully-sealed, mercury-process electrolytic apparatus comprising: an electrolytic cell; a denuding tower; a mercury pump; a sealed main circulation system for mercury through the electrolytic cell, the denuding tower, the mercury pump, and back to the electrolytic cell; overflow separation means disposed outside the main circulation system for removing contaminants from mercury amalgam; means provided in the main circulation system for preventing back-flow of mercury when the mercury pump stops; and means for causing contaminants within the denuded mercury to circulate together with a part of said mercury and mercury wash water, to the denuding tower.

2. The fully-sealed, mercury-process electrolytic apparatus as claimed in claim **1** in which the means for preventing backflow of mercury comprises a side pipe communicatively connecting the denuding tower and the upper part of an elevated part of the main circulation system between the mercury pump and the electrolytic cell.

3. The fully-sealed, mercury-process electrolytic apparatus as claimed in claim in which the means for preventing backflow of mercury comprises an automatically operating valve disposed within the upper part of an elevated part of the main circulation system between the mercury pump and the electrolytic cell and operating to maintain the main circulation system open for passage of mercury therethrough while the mercury pump is operating and to close said system against passage of mercury therethrough simultaneously with the stoppage of the mercury pump.

4. The fully-sealed, mercury-process electrolytic apparatus as claimed in claim **1** in which the means for preventing backflow of mercury comprises a side pipe communicatively connecting the upper part of an elevated part of the main circulation system between the mercury pump and the electrolytic cell to the denuding tower and an automatically operating valve disposed within said elevated part and operating to close passage through the side pipe and open passage through said system while the mercury pump is operating and to open passage through the side pipe and close passage through said system promptly when the mercury pump stops.

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U.S. Cl. X.R.

204—250

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,582,524 Dated June 1st, 1971

Inventor(s) Hiroshi Shibata et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 70, change "desities" to -- densities --.
Column 2, line 31, change "soltuion" to -- solution --.
Column 3, line 52, change "refering" to -- referring --.
Column 4, line 18, change "contamiants" to -- contaminants --; line 62, change "contamiants" to -- contaminants --. Column 5, line 66, change "analgam" to -- amalgam --. Column 7, line 35, after "claim", insert -- 1 --.

Signed and sealed this 18th day of April 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

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