# UNITED STATES PATENT OFFICE.

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## ELECTROLYTIC PROCESS.

No. 798,790. Specification of Letters Patent. Patented Sept. 5, 1905.

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*To all whom it may concern:*

Be it known that I, CARL HERING, a citizen of the United States, residing in the city of Philadelphia and State of Pennsylvania, have invented certain new and useful Improvements in Electrolytic Processes, of which the following is a specification.

In electrolytic processes in which the reaction at one electrode is not the exact reverse of that at the other electrode there is a gradual and progressive change in the electrolyte. This is due to the fact that something is either added to or extracted from the electrolyte or formed or decomposed in it, thereby changing its composition or concentration. In such cases it may happen that the cumulative change thus produced in time interferes with the proper continuance of the desired electrolytic process.

The object of my invention is to provide means by which such objectionable cumulative change in the electrolyte may be prevented, thus enabling the desired process to be continued. This I accomplish by using an electrode of such nature and material as to combine chemically with the objectionable ingredient as it is formed in the electrolyte, thereby rendering it inert as far as the electrolyte is concerned, and thus preventing the latter from being contaminated. In many cases the objectionable ingredient which is thus removed from the electrolyte is a useful product, and my process further contemplates the recovery of this ingredient by removing the electrode with which it has combined and passing the reverse current through it in a second electrolytic process. Thus when it is desired to electrolytically extract a positive ion—say a metal—from a solution containing the same unless the anode is one which continuously replenishes the solution with the metal which is being thrown down at the cathode the negative ion with which the metal is combined may remain in the solution and thus cumulatively hinder the further extraction of the metal. To prevent this setting free and accumulation of the negative ion formerly in combination with the metal, my invention contemplates the use of an anode of such nature and material as upon the passage of the current will chemically combine with this ion to form an insoluble compound, which adheres to or unites with the anode. After the anode has been thus acted upon to its full capacity it may be removed from the solution and placed in another electrolyte and subjected to the action of a current in the reverse sense of that originally employed, thus setting free the combined ion and restoring the plate to its original condition. Furthermore, in many cases the combined ion set free is thus rendered recoverable.

I will now instance certain specific applications of my process, it being understood that they are only examples to illustrate the application of the principle which I have discovered and that my invention is in no way limited to such application.

First. In extracting zinc from a solution of zinc sulfate the presence of an excess of sulfuric acid and the accumulation of the sulfate radical from which the zinc is separated (which forms sulfuric acid when insoluble electrodes are used) hinders the efficient extraction of the zinc. This is because sulfuric acid being less stable than zinc sulfate electrolyzes more readily, setting free hydrogen at the cathode with a consequent loss of energy and also tending to form a loose and spongy instead of a dense and adherent deposit of zinc on the cathode. Furthermore, the presence of the sulfuric acid formed at the anode tends to redissolve the zinc. These phenomena are even more apparent when nearly all of the zinc has been extracted from the solution, as there is then present a relatively large per cent. of sulfuric acid. By the application of my present invention I employ in electrolyzing the zinc-sulfate solution an anode of spongy lead, the cathode being of any material suitable for the deposition of zinc. The sulfate radical as it is set free by the current from the external source then combines with the spongy lead of the anode, forming insoluble lead sulfate, which adheres to the anode and can be removed with it from the solution. After the anode has thus been completely sulfated it is placed in another cell containing water or any other desired electrolyte, and upon being constituted a cathode by a current from an external source in the reverse sense the sulfate radical is again set free with the formation of sulfuric acid, if water be the electrolyte. The spongy-lead anodes must of course be of a capacity corresponding with the quantity of zinc deposited on the cathode in the first operation, or else they must be replaced by new plates from time to time, their exhaustion being indicated by a rise of the voltage between the terminals of the electrolytic cells. It is to be noted that in the first operation, during which the zinc is extracted,

the voltage required to obtain the zinc by my process will be about 1.6 volts less than that theoretically required to extract zinc from its sulfate, as the sulfating of the lead anodes gives rise to a direct electromotive force of this magnitude. This, however, in a continuous process is no gain, as a counter electromotive force of the same amount must be overcome by the current from the external source in the subsequent operation when the anodes are restored to their original condition.

Second. Another application of my process is in the recovery of both zinc and acid from discharged primary-battery cells. Much difficulty has been experienced in extracting the zinc from spent solutions in such cells, as the sulfuric acid, which is always present, besides being formed when the zinc is deposited is decomposed more easily than the zinc sulfate, and much energy is consequently lost in evolving hydrogen. By my process I first extract the free acid, if it is present in sufficient amount to interfere, by electrolyzing the solution between a spongy-lead anode and a peroxid-of-lead cathode. The free acid then combines with both electrodes, forming insoluble products which adhere to the electrodes and may thus be removed. After the free acid has thus been extracted the solution is electrolyzed between a cathode of mercury, zinc amalgam, copper, or any other suitable material for receiving the zinc and an anode of spongy lead, which combines with the acid as fast as it is formed.

Third. A third application of my invention is to the extraction from spent battery-cells of the liquid depolarizer which has diffused through the porous cup or diaphragm of a battery into the compartment containing the exciting liquid. By using a suitable electrode this depolarizer may be made to combine with it and may thereby be removed from the exciting solution and again recovered in a separate receptacle containing the depolarizer solution for the battery by passing a current in the reverse sense through the electrode while it is inserted in this depolarizer solution. It is sometimes advisable to separate the two plates by a porous partition while the depolarizer is thus being extracted in the process of regeneration; but this is not always necessary.

In the common form of primary battery, in which zinc in sulfuric acid and carbon in chromic acid are employed, some of the chromic acid either as such or in the reduced form diffuses into the exciting liquid, and when the liquids are regenerated and used repeatedly this diffused depolarizer would soon accumulate to an objectionable extent. By the application of my improved process the excess of the depolarizing liquid which has diffused into the exciting liquid may be extracted by causing it to combine with a cathode of peroxid of lead during the first part of the process, when the free acid is being extracted from the solution—that is, when a peroxid-of-lead plate and a spongy-lead plate are discharged therein. By what might be called a "primary-battery action" the spongy-lead anode is oxidized by combining with the sulfuric acid, and the peroxid-of-lead cathode is reduced by combining with the chromic acid, both forming insoluble combinations with the electrode, thus enabling these ingredients to be removed from the solutions by removing the electrodes. The peroxid of lead will also combine with the reduced chromium sulfate, apparently by first oxidizing that solution by a purely chemical reaction, and then combining electrochemically with the oxidized chromic acid. The chemical equations for all the parts of the process are given below. To recover this depolarizer, the discharged electrode—as, for instance, the peroxid-of-lead plate in the above specific case—is removed from the solution and is placed in another vessel containing the depolarizing liquid and a reverse current is sent through it, making it the anode. The plate will then become peroxidized again, setting free the depolarizer in the solution from which it originally came. While this is being done the spongy-lead plate, which combined with the sulfuric acid, is reduced again in the solution from which the zinc has been extracted—that is, it is made the cathode—thus giving off the sulfuric acid again in the free state. By this means both plates are simultaneously returned to their original condition and the respective solutions are purified, being kept separated by a porous diaphragm. While the acid is being set free from the sulfated spongy-lead plates as cathodes, the peroxid-of-lead plates, which are then in the discharged depolarizing liquid, separated from the acid solution by a diaphragm, may be used to act as anodes for reoxidizing or regenerating the rest of the depolarizer after they have given off the chromium and the sulfuric acid with which they were combined, as will be understood by those skilled in the art.

The reactions which take place in the various steps of a typical application of my process are believed to be as follows: Taking for illustration the case of the exhausted solution of a zinc-sulfuric acid, chromic acid, carbon battery. This will generally be found to contain some unused sulfuric acid, as well as chromic acid, besides the large quantities of zinc sulfate and chromium sulfate formed during the discharge of the battery. During the first part of the process the free sulfuric acid is taken up by both the spongy lead and the lead-peroxid plates, according to the following reaction:

$$Pb+2(H_2SO_4)+PbO_2=PbSO_4\text{(on lead plate)}+2(H_2O)+PbSO_4\text{(on peroxid plate.)}$$

If any unreduced depolarizer is present, its combination with the peroxid-of-lead plate may be explained by the following equation:

$$Pb+H_2SO_4+H_2CrO_4+PbO_2=PbSO_4+2(H_2O)+PbCrO_4.$$

A peroxid-of-lead plate as soon as it is placed in the reduced depolarizer solution tends to oxidize some of the reduced depolarizer. This seems to be a purely chemical or local action and can be explained by the following equation:

$$Cr_2(SO_4)_3+3PbO_2+2H_2O-2H_2CrO_4+3PbSO_4.$$

The oxidized depolarizer thus formed then combines by what seems to be an electrochemical reaction with some more of the peroxid according to the preceding equation. It will thus be seen that the peroxid of lead seems to act both chemically (or by "local action," as it is sometimes called) and electrochemically.

The reaction taking place when the zinc is deposited is as follows, and it will be seen that one electrode—the cathode of mercury, for instance—receives the zinc in the form of an amalgam, while the $SO_4$, with which the said zinc was in combination, combines with the other electrode, (the anode:)

$$Hg+ZnSO_4+H_2O+Pb=(Hg)Zn+H_2O+PbSO_4.$$

From this it will be seen that no sulfuric acid is set free during the deposition of the zinc, and the extraction of the zinc may therefore be continued to any degree desired without an increased evolution of hydrogen.

As a logical outcome of the above actions it will be understood that the plate having on it lead sulfate may thereafter be treated by passing a current between it and a plate of lead peroxid immersed in an exhausted battery solution containing chromium salts in the green or reduced form, thus simultaneously regenerating the plates and oxidizing the said chromium salts, as shown in the reactions:

$$3PbSO_4+8H_2O+Cr_2(SO_4)_3+3PbO_2=3Pb+6H_2SO_4+2H_2CrO_4+3PbO_2.$$

I am aware that it has long been known that metals may be deposited electrolytically from their solutions upon electrodes, which are subsequently removed, as in electroplating and in the refining of metals. My invention is not so accomplished, but is limited to the formation of a chemical compound by the chemical combination of the material of the electrode and the ion which the electrolysis tends to set free at that electrode, which compound is inert, having no further action in the electrolyte and being therefore, in effect, removed from action. Being insoluble it may be withdrawn by withdrawing this electrode and may therefore be subsequently recovered by a reverse current, if desired; but it will be understood that the prime object of my invention is not the recovery of this ingredient thus removed, but is the removal of it from the electrolyte in order to prevent its objectionable action in hindering a desired electrolysis. It will further be understood that when in this specification and in the claims which follow I speak of an "objectionable" element I do not mean that the element in itself is objectionable or valueless, for in many instances it may be valuable and desirable to recover; but by the word I mean that the element is objectionable so long as it remains in the electrolyte in which it is present or is being formed, because its presence there tends to hinder or prevent the desired electrolysis. My process enables such objectionable elements, whether liquids or gases, to be removed from solutions by their chemical union with the electrode. This is in contradistinction to former processes, in which metals have been removed from solutions by their mechanical adhesion to the electrode, with the further distinction that in such former processes the object of the process was not the elimination from the electrolyte of an objectionable element, but the recovery of the metal.

Having thus described my invention, I claim—

1. In an electrolytic process in which there exists in solution in the electrolyte an ingredient which is objectionable because hindering the desired electrolysis, the method of making such objectionable ingredient inert which consists in electrolyzing the solution with an electrode of a material with which said ingredient will combine to form a chemical compound which is inert in the desired electrolytic process and is thereby removed from further action.

2. In an electrolytic process in which there exists in solution in the electrolyte an ingredient which is objectionable because hindering the desired electrolysis, the method of making such objectionable ingredient inert which consists in electrolyzing the solution with an electrode of a material with which said ingredient will combine to form a chemical compound within the body of the electrode which is inert in the desired electrolytic process and is thereby removed from further action.

3. In an electrolytic process in which there exists in solution in the electrolyte an ingredient which is objectionable because hindering the desired electrolysis, the method of removing and recovering such ingredient which consists in electrolyzing said solution with an electrode of a material with which said ingredient will combine to form a chemical compound which remains on the electrode; removing said electrode with said compound upon it from said solution; and employing it as an electrode in another electrolytic solution with an electric current passing in a direction the reverse of that employed in the first solution whereby said removed ingredient is again set free and recovered.

4. In an electrolytic process in which there exists in solution in the electrolyte an ingredient which is objectionable because hindering

the desired electrolysis, the method of removing and recovering such ingredient which consists in electrolyzing said solution between electrodes the anode of which is formed of a material, with which said ingredient will combine to form a chemical compound which remains on the anode; removing said anode with said compound upon it from said solution; and constituting it a cathode in a suitable electrolyte whereby said compound is again broken up and the removed ingredient recovered.

5. The method of regenerating exhausted battery solutions which consists in electrolyzing the same with the employment of an electrode of such material and a current of such direction as causes the active ingredient of the original exciting battery solution to combine chemically with said electrode and be deposited thereon.

6. The method of regenerating exhausted battery solutions which consists in electrolyzing the same with the employment of an electrode of such material and a current of such direction as causes the active ingredient of the original exciting battery solution to combine chemically with said electrode and be deposited thereon; and thereafter removing said electrode from said solution; and constituting it an electrode in another solution and with a reverse current, whereby the ingredient removed from the first solution is again set free, and the electrode restored to its original condition.

7. The process of removing an excess of free acid from an electrolytic solution containing other electrolyzable elements which consists in employing as anode therein an electrode of a material capable of combining electrolytically with said free acid to form an inert insoluble compound.

8. The process of removing and excluding an excess of free acid from an electrolytic solution containing other electrolyzable elements which consists in employing as anode therein an electrode of a material capable of combining electrolytically with said free acid to form an inert insoluble compound until the excess is removed; and thereafter employing as anode therein an electrode of a material which is capable of entering into chemical combination with the acid radical of the solution.

9. The method of excluding from an electrolytic solution an objectionable ingredient which tends to go into solution therein as a result of the electrolytic process in which the electrolyte is engaged, which consists in employing as anode therein an electrode of a material capable of entering into chemical combination with the objectionable ingredient as it is formed, said chemical combination being an inert solid material.

10. The process of removing an objectionable excess of acid element from a solution of a metallic salt which is being employed as electrolyte for recovery at the cathode of the metallic element, which consists in employing as anode an electrode which is capable of combining chemically and insolubly with the acid radical as it is set free.

11. The process of removing and recovering the objectionable excess of acid element from a solution of a metallic salt, which is being employed as electrolyte for recovery at the cathode of the metallic element, which consists in employing as anode an electrode which is capable of combining chemically and insolubly with the acid radical as it is set free, by the electrolysis; and thereafter removing said electrode, with the acid radical combined with it, and employing it as cathode with another suitable electrolyte in which said acid radical is again set free.

12. The method of facilitating the electrolytic deposition of zinc upon a cathode from an electrolyte containing a zinc salt, which consists in employing as anode, an electrode which will, under electrolysis, form an insoluble chemical compound with the radical with which the zinc was combined.

13. The process of removing the objectionable excess of acid element form a solution of a metallic salt, which is being employed as electrolyte for recovery at the cathode of the metallic element, which consists in employing a mass of spongy lead as anode.

14. The process of removing and recovering the objectionable excess of acid element from a solution of a metallic salt, which is being employed as electrolyte for recovery at the cathode of the metallic element, which consists in employing a mass of spongy lead as anode; and thereafter removing said mass of spongy lead with the acid radical combined with it, and employing it as cathode with another suitable electrolyte in which said acid radical is again set free.

15. The method of facilitating the electrolytic deposition of zinc upon a cathode from an electrolyte containing its salt, which consists in employing with the electrolyte an anode of spongy lead.

16. The process of removing the liquid depolarizer from a spent battery solution which consists in employing an anode therewith of a material capable of combining chemically with the depolarizer and forming a solid and removable deposit thereon.

17. The process of removing and recovering the liquid depolarizer from spent battery solutions which consists in employing an anode therewith of a material capable of combining chemically with the depolarizer and thereafter removing said anode combined with the depolarizer, and converting it into a cathode in combination with another electrolyte.

18. The process of reclaiming free acid and depolarizer from exhausted battery solutions containing both free acid and depolarizer which consists in immersing in such solution electrodes of such material that a portion of

the free acid and the depolarizer combine chemically with one electrode, forming inert solid compounds on the electrode; and the remainder of the free acid combines chemically with the other electrode; removing the said electrodes from said solution and immersing them in a second solution with interposition of a porous diaphragm and with a reverse current whereby said electrodes are restored to their original condition, and free acid and liquid depolarizer reclaimed.

19. The process of reclaiming free acid and depolarizer from a mixture of exhausted liquid depolarizer and exhausted exciting fluid containing free acid, resulting from the operation of a two-liquid primary battery, which consists in electrolyzing the same with an anode of spongy lead, and a cathode of lead peroxid whereby the free acid combines chemically with the anode, and the depolarizer combines chemically with the cathode forming inert solid compounds on the electrodes, removing said electrodes from said solution; and immersing them in a second solution with interposition of a porous diaphragm and with a reversed current, whereby said electrodes are returned to their original condition, and free acid and depolarizer reclaimed.

20. The process of electrodepositing zinc which consists in electrolyzing a solution of zinc sulfate with a suitable cathode, and an anode of spongy lead.

21. The process of electrodepositing metals of greater chemical affinity than lead, which consists in electrolyzing their sulfate solutions with a suitable cathode, and with an anode of spongy lead.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

CARL HERING.

Witnesses:
JOS. H. KLEIN,
WILLIAM E. BRADLEY.

Correction in Letters Patent No. 798,790.

It is hereby certified that in Letters Patent No. 798,790, granted September 5, 1905, upon the application of Carl Hering, of Philadelphia, Pennsylvania, for an improvement in "Electrolytic Processes," an error appears in the printed specification requiring correction, as follows: In the chemical equation, line 8, page 3, the minus sign (—) should be the sign of equality (=); and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 3rd day of October, A. D., 1905.

[SEAL.]

F. I. ALLEN,
*Commissioner of Patents.*

the free acid and the depolarizer combine chemically with one electrode, forming inert solid compounds on the electrode; and the remainder of the free acid combines chemically with the other electrode; removing the said electrodes from said solution and immersing them in a second solution with interposition of a porous diaphragm and with a reverse current whereby said electrodes are restored to their original condition, and free acid and liquid depolarizer reclaimed.

19. The process of reclaiming free acid and depolarizer from a mixture of exhausted liquid depolarizer and exhausted exciting fluid containing free acid, resulting from the operation of a two-liquid primary battery, which consists in electrolyzing the same with an anode of spongy lead, and a cathode of lead peroxid whereby the free acid combines chemically with the anode, and the depolarizer combines chemically with the cathode forming inert solid compounds on the electrodes, removing said electrodes from said solution; and immersing them in a second solution with interposition of a porous diaphragm and with a reversed current, whereby said electrodes are returned to their original condition, and free acid and depolarizer reclaimed.

20. The process of electrodepositing zinc which consists in electrolyzing a solution of zinc sulfate with a suitable cathode, and an anode of spongy lead.

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