

V. ENGELHARDT & M. HUTH.
ELECTROLYTIC WINNING OF ZINC FROM SOLUTIONS OF ZINC SULFATE.
APPLICATION FILED MAY 25, 1907.

935,250.

Patented Sept. 28, 1909.

Fig. 1

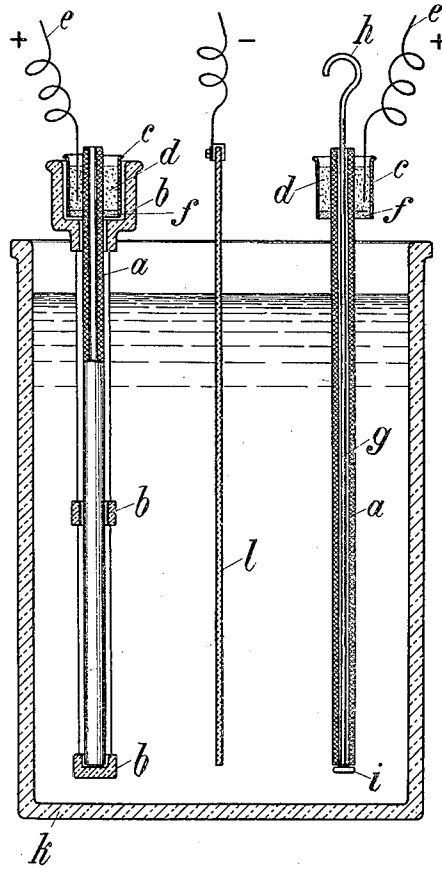
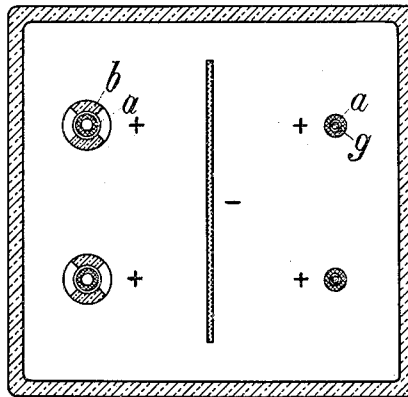


Fig. 2



Witnesses:
Ray J. Anet.
Octavius Hughes.

Victor Engelhardt,
Max Huth, Inventors.
by Knight Bros. Attorneys

UNITED STATES PATENT OFFICE.

VICTOR ENGELHARDT AND MAX HUTH, OF CHARLOTTENBURG, GERMANY, ASSIGNORS
TO SIEMENS & HALSKE, AKTIENGESSELLSCHAFT, OF BERLIN, GERMANY, A COR-
PORATION OF GERMANY.

ELECTROLYTIC WINNING OF ZINC FROM SOLUTIONS OF ZINC SULFATE.

935,250.

Specification of Letters Patent. Patented Sept. 28, 1909.

Application filed May 25, 1907. Serial No. 375,704.

To all whom it may concern:

Be it known that we, VICTOR ENGELHARDT, a subject of the Emperor of Austria-Hungary, and MAX HUTH, a subject of the German Emperor, residents of Charlottenburg, near Berlin, Germany, have invented a certain new and useful Improvement in Electrolytic Winning of Zinc from Solutions of Zinc Sulfate, of which the following is a specification.

The present invention relates to improvements in the electrolytic winning of zinc from solutions of zinc sulfate.

In the electrolysis of zinc sulfate solutions without using a diaphragm, the electrolyte becomes gradually richer in free sulfuric acid, so that in a short time the content of acid is so great that the deposited zinc dissolves again although the electrolyte is still comparatively rich in zinc.

An important object of the present invention is to permit the content of sulfuric acid in the electrolyte being very high without ill effect by using a sufficiently pure solution of zinc sulfate and by preventing access of any impurities to the electrolyte during the process.

The deposition of the zinc from strongly acid solutions has the advantage that the deposited zinc is beautifully crystalline and completely free from oxid, and that it is possible to deposit the zinc very nearly completely from comparatively concentrated solutions. This procedure has not hitherto been possible for want of a suitable anode material. The known anodes may be catalogued as follows:—1. Platinum and its alloys. 2. Hard lead which becomes covered with peroxid and thus acts as a peroxid electrode. 3. Soft lead plates which act like hard lead. 4. Positive accumulator plates, which have been previously covered with peroxid by a forming process. 5. Carbon, which however is wholly inapplicable for electrolysis of sulfate. All these electrodes have the disadvantage that during the electrolysis small quantities of the respective metal dissolve and render the electrolyte so impure that it is not possible to permit the concentration of the acid to become high, because the deposited zinc dissolves again.

Platinum anodes are always attacked in sulfate solutions, particularly in presence of organic acids. The quantity thus dissolved

is indeed so small that frequently it can be detected in the electrolyte by analysis with difficulty or not at all; all the same, this small proportion suffices to accelerate very considerably the dissolution of the zinc. When hard or soft lead, or accumulator plates are used, lead always dissolves as sulfate, and in the case of hard lead antimony also. Although lead, platinum or antimony are frequently not to be analytically detected in the electrolyte one of the metals can always be found in the cathode deposit. This deposit of impure zinc, however, is much more easily soluble in acid than quite pure zinc is.

According to the present invention, if as anode, pure massive or compact lead peroxid be used such as separates on the anode during the electrolysis of solutions of lead salts, and if every other metal and even carbon be completely excluded the content of free sulfuric acid may be allowed to exceed 10 per cent. without conversion or dissolution of the zinc already deposited. The lead peroxid must not be carried upon a metal support, but may be supported by a non-conductor of electricity which is not attacked by the electrolyte. When using such anodes, the peroxid being not porous but massive, and not being carried on a metallic support, lead cannot be detected either in the electrolyte or in the zinc deposited on the cathode, this is an indication that in other cases the foreign metal dissolved at the anode is actually the cause of the dissolution of the zinc already deposited.

In order that the invention may be more clearly understood I have illustrated in the accompanying drawing two forms of anodes showing the means of employing the lead peroxid and supporting the same for practical use as an anode.

Figure 1 is a vertical sectional view of two forms of anode embodying the invention, and Fig. 2 is a transverse sectional view of the same.

It will be understood that the form and the manner of mounting the anode will be determined by the use or purpose for which it is intended. In the examples illustrated in the drawing *a* indicates a rod-like anode formed of lead peroxid supported in a protective sheath *b* of stone (earthen) ware or other similar material which is provided

with openings *m* through which the peroxid is exposed to the action of the electrolyte. The upper end of the protective sheath *b* has a cup-like formation, as shown in the drawing. The terminal connection is formed by means of a cylindrical sheath *c* arranged within the cup-like part and having a base or bottom *f* consisting of a cork disk or of asbestos cord or other suitable material, through which passes the electrode *a*. This sheath *c* and its bottom *f* form a receptacle into which and around the electrode *a* is poured an easily fusible contact metal or alloy *d* in which the conductor *c* is embedded.

A modified form of anode is shown to the right of Fig. 1 in which the lead peroxid anode is formed about a glass rod *g* which thus constitutes a core. This core is provided with a bottom flange or foot piece *i* to protect the peroxid anode material. This glass rod *g* is provided with a hook *h* for convenient hanging on a support. The conductor *e* may be attached to the anode in a manner similar to that already described for the first modification. The cathode is represented by reference letter *l* and the cell by *k*. The lead peroxid suitable for the anode is, as above stated, that which is obtained from the electrolysis of solutions of lead salts. As examples, the lead peroxid which is deposited on the anode from solutions of easily soluble lead salts, such as the nitrate or perchlorate may be mentioned.

The herein described invention permits the obtaining of a good deposition of zinc, free from impurities and of a dense crystalline character. It also enables the obtaining of a very nearly complete recovery of the zinc of the electrolyte, and makes possible the use of strongly acid solutions for the electrolyte.

Where the anode material is mounted upon or in supports which are affected or attacked by the electrolyte, as for instance where lead accumulator or battery plates or grids are employed, the electrolyte, particularly when its content of acid has increased, attacks the support or grid, penetrating the pores of the peroxid and takes up lead and other impurities. This not only results in an impure deposit on the cathode, but the presence of the impurities causes the deposit to be readily re-dissolved in the electrolyte; since, while pure zinc resists the action of

the acid, impurities therein even though small in amount render it readily soluble. Even were the peroxid layer free from pores, the slightest check or crack therein would afford entry for the electrolyte to the support. Further, the lead peroxid of accumulator plates always contains lead sulfate, since the oxidation of the paste to peroxid is never perfect, some lead sulfate being formed. This lead sulfate is decomposed in the electrolysis and the zinc deposit thus becomes not only contaminated with deposited lead but is also made soluble in the electrolyte. By employing a lead peroxid anode, which is non-porous, so as to have good conductivity, and which is free from constituents or parts attackable by the electrolyte, a high recovery of zinc from strongly acid electrolyte and a good deposit may be obtained.

What we claim as our invention and desire to secure by Letters Patent is:

1. The process of obtaining zinc electrolytically from sulfate solutions which consists in employing an anode of lead peroxid in compact form and free from constituents or parts attackable by the electrolyte.

2. In the process of electrolytically obtaining zinc from sulfate solutions, the process of preventing re-dissolution of the zinc deposit which consists in employing for the electrolysis an anode of compact lead peroxid free from constituents soluble in the electrolyte.

3. The process of obtaining zinc electrolytically from strongly acid sulfate solutions which consists in employing for the electrolysis an anode of electrolytic lead peroxid free from metallic parts or constituents.

4. The process of obtaining zinc electrolytically, which consists in subjecting zinc sulfate solution to the action of the electric current passing from an anode of compact lead peroxid free from constituents or parts attackable by the electrolyte to a cathode.

In testimony whereof we have signed our names to this specification in the presence of the two subscribing witnesses.

VICTOR ENGELHARDT.
MAX HUTH.

Witnesses:

WOLDEMAR HAUPT,
HENRY HASPER.