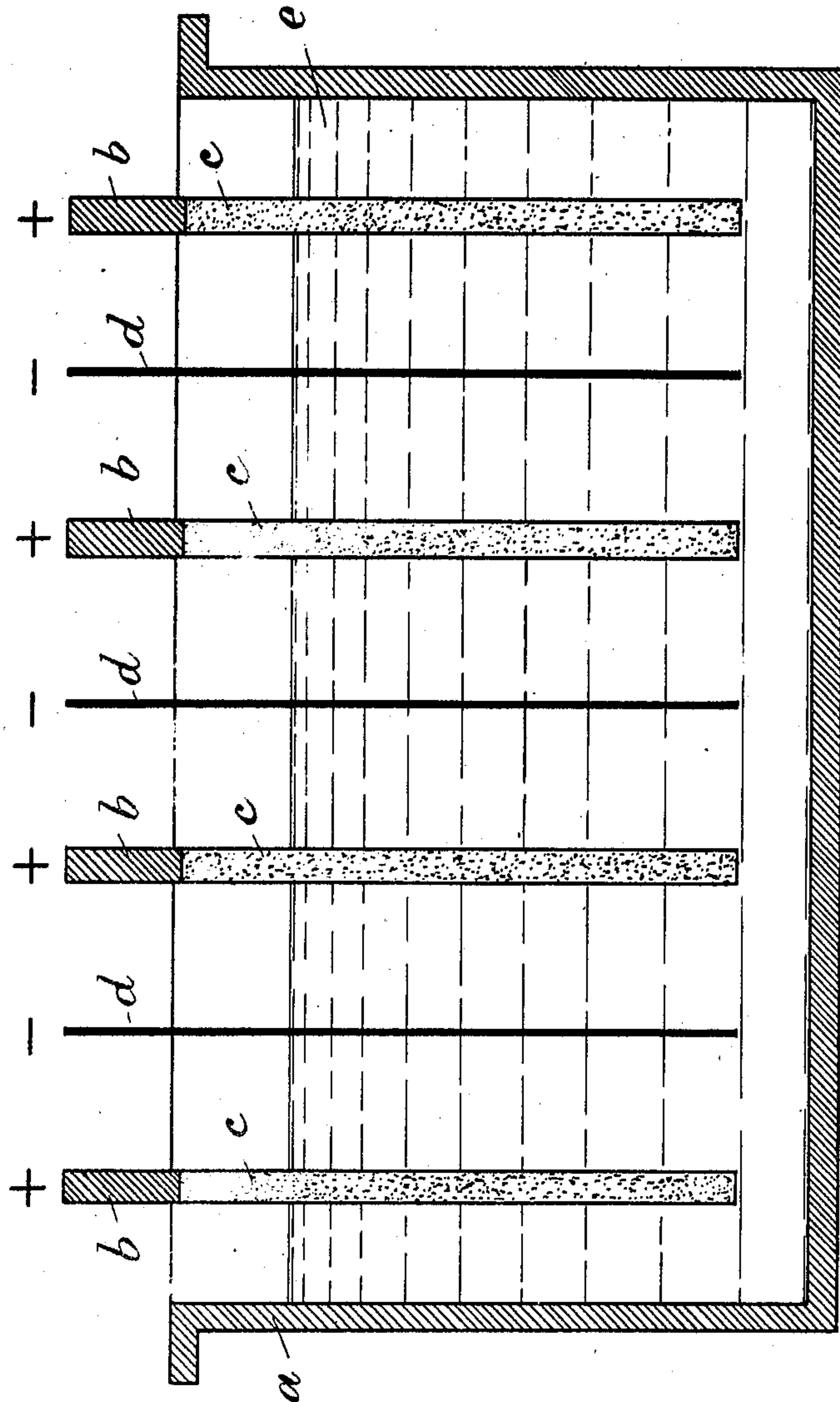


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 APPARATUS FOR THE ELECTROLYSIS OF AQUEOUS SOLUTIONS.
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935,109.

Patented Sept. 28, 1909



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APPARATUS FOR THE ELECTROLYSIS OF AQUEOUS SOLUTIONS.

935,109.

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

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To all whom it may concern:

Be it known that I, MAX HUTH, a subject of the German Emperor, and residing at Charlottenburg, near Berlin, Germany, have
5 invented certain new and useful Improvements in Apparatus for the Electrolysis of Aqueous Solutions, of which the following is a specification.

The present invention relates to apparatus
10 for the electrolysis of aqueous solutions, such as solutions of zinc sulfate, nitrate of copper, sodium chlorid or the like, which may also contain free acid.

When electrolyzing aqueous solutions in
15 general and particularly aqueous solutions of salts, it is preferable for the anode to consist of a material which cannot be attacked chemically. It has already been proposed to make the anode of peroxid of lead for
20 such purposes. The employment of such anodes has also proved successful, but the employment of these peroxid of lead anodes is limited, having regard to the employment heretofore in the form of rods. Also it is
25 frequently disadvantageous when lead ions pass into the solution from the peroxid of lead on account of reduction which occurs under certain circumstances.

Now in accordance with the present in-
30 vention instead of peroxid of lead, peroxid of manganese is used as anode in a solid form which is obtained artificially. Crystalline peroxid of manganese conducts electric current well and can be brought readily into
35 the form of rods or plates. In addition it has the great advantage that, when reduction does take place under certain circumstances, only manganese ions pass into the solution and these have no injurious effect on the
40 deposition of metal at the cathode.

It has already been attempted to employ peroxid of manganese electrodes, namely, for example, in the form of a sheet of platinum coated electrolytically with amorphous per-
45 oxid of manganese. Peroxid of manganese electrodes made in this manner cannot be employed as anodes, however, since this peroxid of manganese has the property of being converted in dilute sulfuric acid by the elec-
50 tric current into higher degrees of oxidation which are soluble in water. The highest degree of oxidation of manganese, permanganic acid, is most readily formed in this manner. Further, it has been proposed to use natural

manganese ore in the form of pieces or lumps 55
and to conduct the current to these anodes by means of carbon rods. But these anodes also have a number of disadvantages. Namely, when electrolyzing aqueous solu-
60 tions by means of so-called "insoluble anodes" disadvantages frequently occur on account of impurities passing into the electrolyte from the anode material owing to chemical or anodic solvent actions. Conse-
65 quently, as a rule, the cathode products are of inferior quality and also the anode material is destroyed more rapidly. Such results are particularly noticeable in the electrolysis of zinc sulfate solutions, in which
70 any metal which is more electronegative than zinc must be carefully prevented from passing into the electrolyte. Natural manganese ore always contains such impurities, how-
75 ever, so that it is entirely useless for the electrolysis of zinc sulfate solutions. Moreover, when natural manganese ore is employed conductors to the separate pieces of
80 the same must always be used, such as, for example, carbon rods or the like. The destruction of these conductors below the surface of the liquid is unavoidable.

In contradistinction to the above it has been found that crystalline peroxid of man-
85 ganese, such as is formed by heating manganese nitrate or in similar manner, possesses sufficient mechanical strength to be employed in solid form and without sup-
90 porting sheet metal insertions or the like. Further, it has been found that this crystalline peroxid of manganese is either not oxidized higher at all or only to a very in-
95 significant extent in sulfate solutions and the like during the electrolysis, for example when used as anode in dilute sulfuric acid. In so far as oxidation does occur at
100 all the same takes place only when freshly made electrodes are first used, and is to be attributed to the freshly made peroxid of manganese electrodes containing amorphous
105 peroxid of manganese or manganese of other degrees of oxidation, if to only a small extent. But in themselves peroxid of manganese electrodes are to be looked upon as anodes which cannot be attacked, that is to say oxygen escapes at the anode when sul-
furic acid is electrolyzed for example, and at most a very small fraction of the electric current employed is consumed in attacking

the anode. Further, under certain circumstances it is advantageous to impregnate the peroxid of manganese electrode with pore-closing, means which cannot be attacked, such as ceresin, paraffin or the like. The electrolyte does not then penetrate into the pores of the electrode, so that consequently the place of contact is protected from the action of the electrolyte, and on the other hand the electrolyte is also protected from impurities. Under certain circumstances it suffices to treat in this manner only one strip of the electrode a few centimeters broad bounding the place of contact.

The peroxid of manganese electrode suitable for the present process can be made, for example, by pure nitrate of manganese being heated to 150° to 200° C. in molds which are attacked neither by the molten mass produced nor by the gases which are formed. The peroxid of manganese separates as a solid coherent mass, it being given the form of the vessel which is used. The duration of the heating depends, of course, on the size of the electrodes which are to be produced. Under certain circumstances it may be preferable to press crystalline peroxid of manganese into molds mechanically, in which case nitrate of manganese may be used as a binding agent, the mass being then heated if desired. In this manner, besides pure crystalline peroxid of manganese, old, already used electrodes can be worked up after suitable preparation for employment as anodes. Thus it is possible to obtain peroxid of manganese both in rods and in plates according to the requirements in each instance.

Owing to this fact and owing to peroxid of manganese electrodes when employed as anodes having the advantage that they can send only manganese ions into solution as mentioned above, in the event of reduction occurring such anodes can be used with advantage for the electrolysis of zinc from aqueous sulfate solutions. For as no metal which is more electronegative than zinc can pass into the solution, even if the anode is attacked such electrolysis will succeed. As one important advantage of the process it has been found that when pure massive peroxid of manganese is employed as anode and when in addition care is taken that metal ions do not go into solution from the places of contact, a concentration of acid up to over 10% free sulfuric acid can be worked

with without the already deposited zinc being corroded or redissolved.

I have illustrated in the accompanying drawing a trough containing the electrodes described before. In this drawing *a* represents the trough containing the electrolyte *e*.

c represents the peroxid of manganese electrodes to the upper end of which carbon bindings *b* are fastened.

d represents the cathode.

What I claim as my invention and desire to secure by Letters Patent is:

1. In an apparatus for the electrolysis of aqueous solutions such as zinc sulfate solutions or solutions of other sulfates, an anode consisting of massive, artificially produced peroxid of manganese.

2. In an apparatus for the electrolysis of aqueous solutions such as zinc sulfate solutions or solutions of other sulfates, an anode consisting of massive, artificially produced peroxid of manganese free from constituents susceptible to the action of the electrolyte.

3. In an apparatus for the electrolysis of aqueous solutions such as zinc sulfate solutions or solutions of other sulfates, an anode consisting of massive, artificially produced peroxid of manganese coated with ceresin.

4. The herein described process of producing massive peroxid of manganese anodes for electrolyzing aqueous solutions which consists in heating pure nitrate of manganese in molds.

5. The herein described process of producing massive peroxid of manganese anodes for electrolyzing aqueous solutions which consists in mixing crystalline peroxid of manganese with a binding agent, in pressing the mixture thus obtained into molds and heating the same therein.

6. The herein described process of producing massive peroxid of manganese anodes for electrolyzing aqueous solutions which consists in mixing crystalline peroxid of manganese with nitrate of manganese, in pressing the mixture thus obtained into molds and heating the same therein, as set forth.

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

MAX HUTH.

Witnesses:

HENRY HASPER,
WOLDEMAR HAUPT.