

(No Model.)

H. BLACKMAN.  
ELECTROLYTIC ANODE AND APPARATUS.

No. 568,231.

Patented Sept. 22, 1896.

FIG. 1.

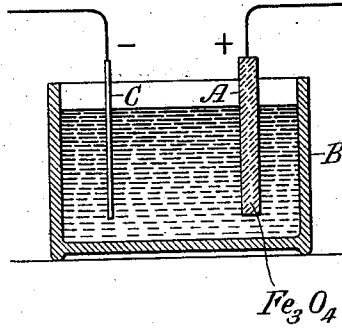
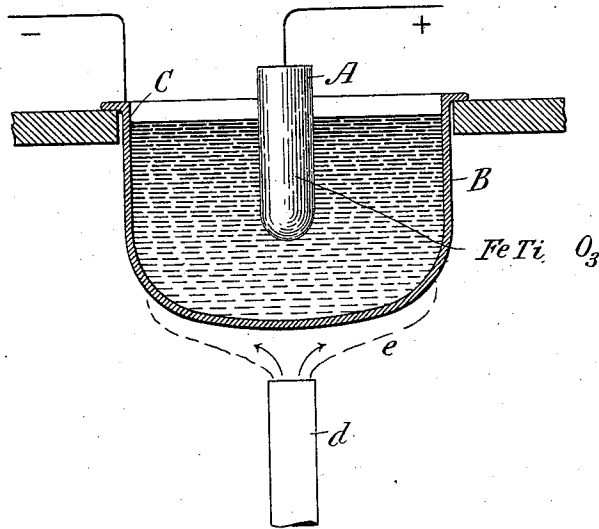


FIG. 2.



WITNESSES:

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# UNITED STATES PATENT OFFICE.

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## ELECTROLYTIC ANODE AND APPARATUS.

SPECIFICATION forming part of Letters Patent No. 568,231, dated September 22, 1896.

Application filed May 21, 1895. Serial No. 550,104. (No model.)

*To all whom it may concern:*

Be it known that I, HENRY BLACKMAN, a citizen of the United States, residing in the city, county, and State of New York, have invented certain new and useful Improvements in Electrolytic Anodes and Apparatus, of which the following is a specification.

This invention relates to anodes for electrolytic decompositions, of which the electrolysis of sodium chlorid is a type. Sodium chlorid may be electrolyzed in the form of an aqueous solution or brine or when liquefied by fusion. In either case chlorin is liberated at the anode and sodium at the cathode. In the case of an aqueous solution the sodium decomposes water and unites with the oxygen and one atom of hydrogen to form sodium hydroxid or caustic soda, and the other atom of hydrogen is set free. For the manufacture of chlorin and caustic soda these two products are kept separated after their formation in the electrolytic cell. For the manufacture of "electric bleach," so called, no separation is effected, and a reaction occurs whereby sodium hypochlorite ( $\text{NaClO}$ ) is formed, which has important bleaching properties. In such electrolytic decompositions much difficulty has been experienced by reason of the rapid destruction of the anode during the electrolytic action. The substances with which most success has been attained are refractory-retort carbon and platinum. The carbon, however, has the disadvantage of disintegrating and disengaging particles or specks in the electrolyte, which greatly impairs it, particularly in the case of bleaching solutions. Platinum plates are excessively expensive and in course of time become corroded or dissolved by the electrolytic action. Plates of prepared peroxid of lead have also been used, but are very expensive of preparation, are very imperfect conductors, and are excessively heavy. The desirable properties for an electrolytic anode for such uses are, first, that it shall be unacted upon by the electrolyte or the products of electrolysis; second, that it shall be a good electric conductor; third, that it shall be reasonably cheap, and, fourth, that it shall not be so heavy as to render the necessary handling of the plates burdensome.

The object of my present invention is to provide means for effecting such electrolytic

decompositions without encountering the disadvantages heretofore experienced.

In accordance with my invention the required decomposition is effected by passing a current from an extraneous source into the electrolyte from an anode of an electroconductive oxid of iron in a dense impermeable mass, substantially resistant to such products of electrolysis of chlorin compounds as are liberated at the anode, that is, the electro-negative products of such electrolysis. Magnetic iron oxid or magnetite ( $\text{Fe}_3\text{O}_4$ ) and iron titanium oxid or ilmenite, the formula for which is given by Watts as  $\text{FeTiO}_3$  and by Roscoe and Schorlemmer as  $(\text{FeTi})_2\text{O}_3$ , are examples of such electroconductive oxid of iron. These oxid are almost wholly unacted upon during the electrolysis of an aqueous solution of sodium chlorid. They have the advantage of being good conductors and when used as the anode do not speck or discolor the electrolyte and have great durability against corrosion and disintegration by the electrolytic action. In this respect my experience with them indicates that the longer they are used the less they are affected. They also have the advantage that their specific gravity is not great, so that electrodes made from them are not inconveniently heavy to handle. They are also very cheap.

In electrolytic bleaching as ordinarily practiced, that is, by electrolyzing brine, using carbon as the anode, it is found that even with the most refractory carbon there is a continual disintegration of the carbon, disengaging in the resulting bleaching solution fine particles or specks of carbon, which it has been found almost impossible to remove by filtration or otherwise, so that when the solution is employed for bleaching paper-pulp, for example, the pulp is found to be slightly discolored by the minute specks of carbon which are deposited upon it. With an anode of magnetite or ilmenite instead of carbon the specking or discoloration of the solution is reduced to such an extent as to be practically insignificant.

The accompanying drawings illustrate two forms of electrolytic apparatus embodying my invention.

Figure 1 is a vertical section of an electrolytic cell B, with an anode A, of magnetite,

and a cathode C, of any suitable material, adapted to withstand the action of the electrolyte during electrolysis. Fig. 2 is a section of an electrolytic cell B, of metal, and connected in the circuit, so that its inner surface C serves as the cathode and an anode A of ilmenite.

My invention may be used with an electrolyte consisting of an aqueous solution of a chlorid or other salt or compound to be decomposed. Fig. 1 may be understood as showing such a solution.

My invention is also applicable with molten or fused electrolytes, such as fused sodium chlorid. The electrolyte may be fused by heat externally applied to the cell or receptacle, this being shown in Fig. 2, where a Bunsen burner *d* is arranged beneath the cell to direct its flame *e* against it; or the electrolyte may be fused or kept fused by electric heat in case it offers sufficient resistance to the passage of the current through it to generate sufficient heat to keep it fused. In this case the burner *d* may be omitted from Fig. 2.

The iron or analogous oxids (as magnetite or ilmenite) may be used in the form in which they occur as minerals by sawing, chipping, or otherwise shaping the mineral into a slab, cylinder, or other desired shape; or it is within my invention to cast the oxid into the desired shape for the electrode by adding to it a sufficient proportion of suitable fluxing agents, such as silica, lime, and magnesia, to enable it to be fused and caused to flow, but such fluxes, being non-conductors, should not be in such large proportion as to materially impair the electric conductivity of the electrode. An electrode of such composition of magnetic iron oxid and a flux is claimed in my application, Serial No. 537,805, filed February 9, 1895. An electrode of ilmenite is claimed in my application, Serial No. 548,722, filed May 9, 1895.

My invention may be modified by mixing or fusing together the magnetite and ilmenite, either with or without other materials or substances, such as fluxing agents.

My invention may be further modified by pulverizing the oxid and compacting it into a cake, slab, or other form by heavy pressure or by the use of any binding material, such,

for example, as tar or sugar, and then pressing it into the desired form by heavy pressure and afterward drying or baking the resulting cake, the binding agent in any such case being preferably so insignificant in proportion that if subject to disintegration it cannot seriously discolor the electrolyte.

I do not wish to be understood as limiting my invention in its application solely to the electrolysis of chlorin compounds, as it may be equally applicable with other compounds or solutions as the electrolyte, being especially advantageous in any case where the electrolytic process develops a powerful oxidizing action at the anode.

My invention is not limited to the anode being homogeneous throughout, as the portions of the anode which are not in contact with the electrolyte might be of other materials than those essential to my invention if found advantageous. For example, it might be found practicable to employ as the anode an iron plate heavily covered or coated with a dense impermeable layer of such an electroconductive oxid as is essential to my invention wherever the anode comes in contact with the electrolyte.

I claim as my invention the following-defined novel features, substantially as hereinbefore specified, namely:

1. An anode for use in electrolytic decomposition consisting of electroconductive oxid of iron in a dense impermeable mass, substantially as set forth.

2. The combination in an electrolytic apparatus, with an extraneous source of electric current, of a receptacle for the electrolyte, a cathode, and an anode the exposed surface of which is a dense impermeable electroconductive iron oxid, substantially as specified.

3. The combination in an electrolytic apparatus, with a receptacle for the electrolyte and a cathode, of an anode consisting of dense impermeable magnetic iron oxid.

In witness whereof I have hereunto signed my name in the presence of two subscribing witnesses.

HENRY BLACKMAN.

Witnesses:

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LUCIUS PITKIN.