

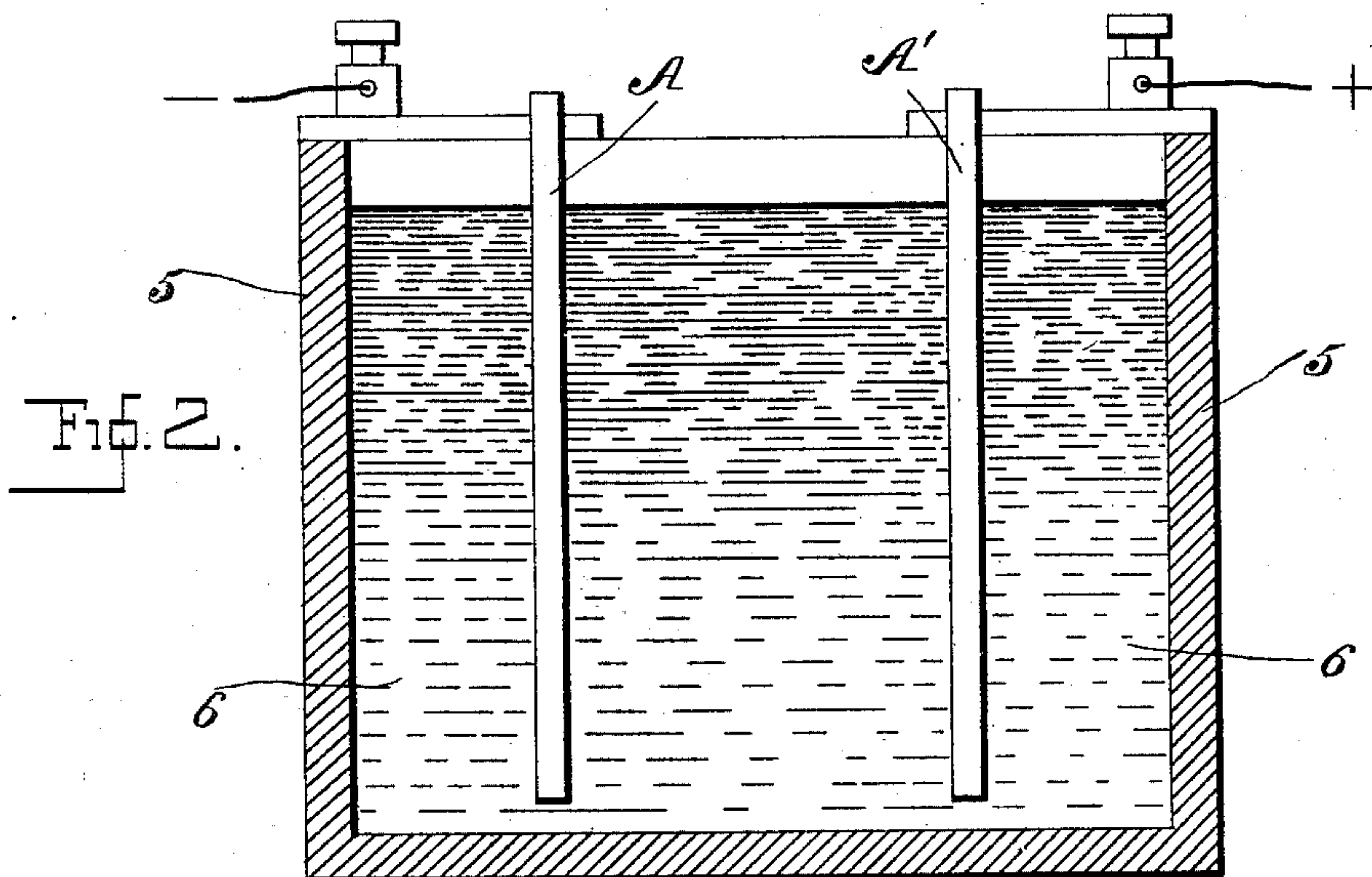
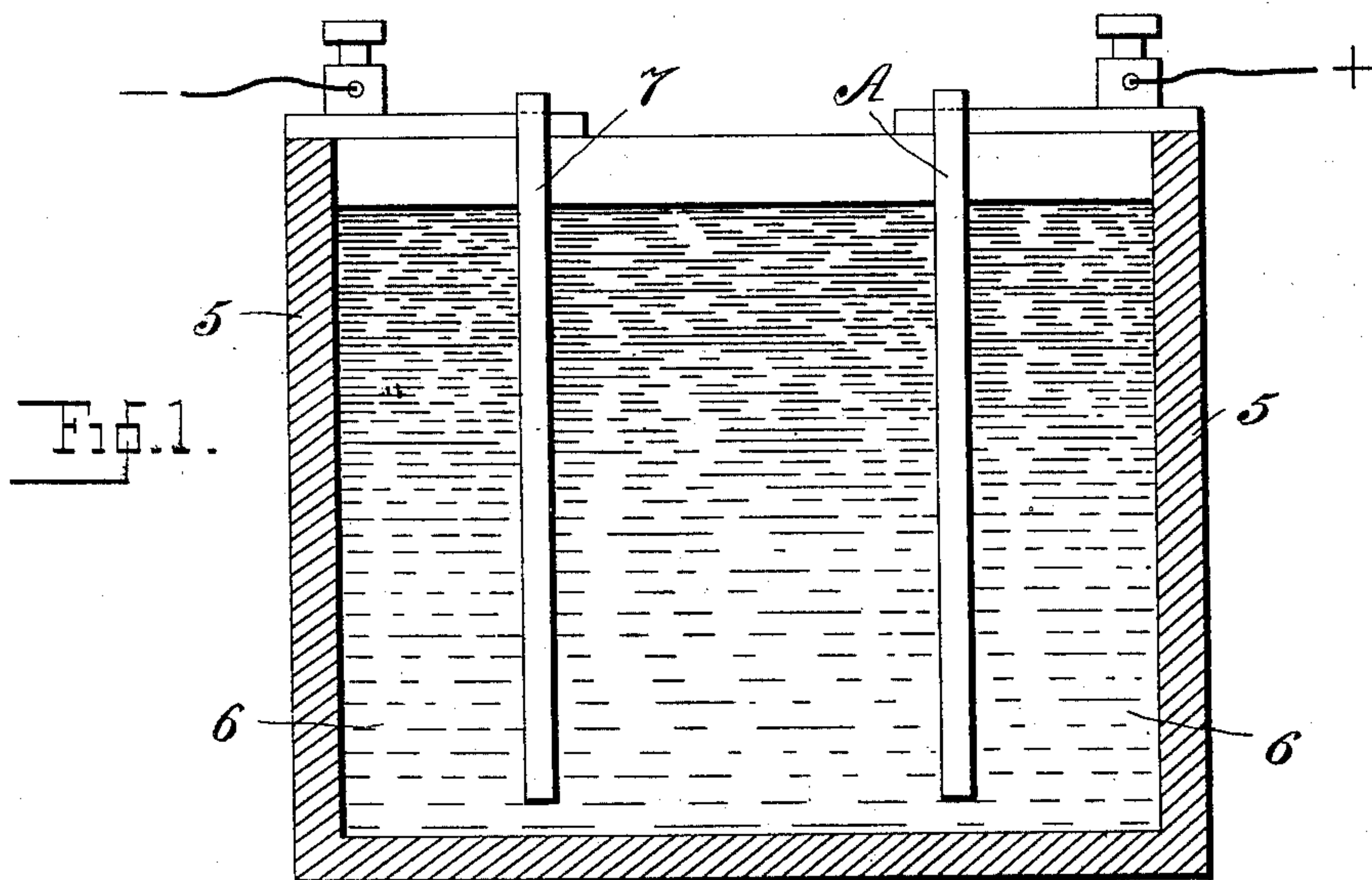
No. 699,492.

Patented May 6, 1902.

R. N. CHAMBERLAIN.
PROCESS OF FORMING STORAGE BATTERY PLATES.

(Application filed Nov. 9, 1900.)

(No Model.)



Witnesses.
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UNITED STATES PATENT OFFICE.

RUFUS N. CHAMBERLAIN, OF DEPEW, NEW YORK, ASSIGNOR TO GOULD STORAGE BATTERY COMPANY, OF NEW YORK, N. Y., A CORPORATION OF WEST VIRGINIA.

PROCESS OF FORMING STORAGE-BATTERY PLATES.

SPECIFICATION forming part of Letters Patent No. 699,492, dated May 6, 1902.

Original application filed March 3, 1899, Serial No. 707,592. Divided and this application filed November 9, 1900. Serial No. 35,981. (No specimens.)

To all whom it may concern:

Be it known that I, RUFUS N. CHAMBERLAIN, a citizen of the United States, residing at Depew, Erie county, and State of New York, have invented certain new and useful Improvements in Processes of Forming Storage-Battery Plates, of which the following is a specification.

This invention relates to an improvement in processes of forming storage-battery plates, and particularly to forming plates which have previously been subjected to pickling in an electrolytic bath, so as to cleanse the surface from impurities and develop a rough or grain surface.

I have found that the pickling of lead storage-battery plates preparatory to forming them is greatly facilitated and nearly a complete saving of lead and of the pickling agent is effected by constituting the plate the anode in an electrolytic bath containing the pickling agent, such as a solution of nitric acid, and collecting on the cathode of such bath the lead which has been dissolved by the pickling solution and electrolytic action of the current. The object of the pickling is, first, to remove the superficial glaze or surface of the lead plate and develop a rough or grain surface thereon, and, second, to remove from the plate as far as possible the impurities which are more soluble than the lead. The process of pickling plates with the aid of electrolytic action is described and claimed in my application, No. 707,592, filed March 3, 1899, of which this application is a division.

From the pickling-bath the plates are removed to the forming-bath, each plate being first constituted the anode in such bath, so as to receive a coating of oxid, and then being constituted the cathode in the same or a similar bath, a fresh plate being then made the anode, so that the reduction of the oxidized coating on the first plate serves to diminish the amount of energy required to form a coating of oxid on the second plate. In this connection I prefer to use in the forming-bath a solution that is not reduced in any substantial degree by the electrolytic action at the cathode-plate. The same solution may then

be used for a very much longer time than a solution which is reducible under such circumstances. The use of such an irreducible solution would involve considerable expenditure of energy in the generation of free hydrogen at the cathode if it were not for the presence at such cathode of the previously-oxidized coating, which prevents evolution of hydrogen and correspondingly diminishes the counter electromotive force or polarization of the forming-bath. The solution used in the forming-bath is also of such a character that the formation of the oxidized coating on the lead plates is of a chemical rather than electrolytic nature. The thickness of oxid produced by an electrolytic charge according to the Planté process is very limited, and it is only by a great number of successive charges and discharges that a sufficient thickness or depth of oxidation can be procured to give even a moderate capacity. By a chemical formation, however, the coating of oxidized material can be formed to sufficient thickness at a single charge, the formation being due to a series of successive solutions and precipitation due to the reactions of the solvent and the electric current being used mainly to hasten and localize the chemical action. The solution I use for thus forming the plates is preferably a mixed dilute solution of acetic and sulfuric acids in water.

One result of the second step in the above-described forming process—namely, of the exposure of the plate as the cathode in the forming-bath—is the reduction of the coating on the plate to the metallic state. All the plates thus leave the forming-bath in the metallic state whether they are eventually intended for positives or negatives, and in this state they can be handled with less liability of injury than when in the oxidized state. The effect of the electrolytic action on the plate while it is exposed as a cathode is also to more or less completely remove or neutralize the acidic elements remaining in the plate from the previous pickling and oxidizing processes. This results partly from the electrolytic movement of electronegative or acidic

ions away from the cathode-plate and partly from the reducing or neutralizing effect of the hydrogen evolved. To render this effect more complete, the electrolytic action may be continued after the complete reduction of the oxidized plate, so that hydrogen is freely evolved and a strong cleansing action is thus produced.

The method of cleaning spongy lead plates for storage batteries in an acid-bath by the aid of electrolytic action I have made the subject of another divisional application, Serial No. 35,982, filed November 9, 1900.

In the accompanying drawings, Figures 1 and 2 are diagrammatic representations, in vertical section, of the forming-vat, illustrating two successive operations in my method of forming storage-battery plates, hereinafter described and claimed.

Each plate after it has been sufficiently pickled is removed to the forming-vat, (shown at 5 in Fig. 1,) which contains a bath (indicated at 6) consisting of a solution of about three per cent. of acetic acid and about ten per cent. of sulfuric acid in water. Thus the plate A is placed in such bath and exposed to electrolytic action as an anode. The effect of the action of the solution on such plate is to form a coherent substantial deposit or coating of oxidized material on the surface of the plate. This action may be explained as follows: The acetic acid dissolves some of the superficial portion of the lead plate, forming lead acetate; but as soon as this solution is formed it is decomposed by the sulfuric acid, forming sulfate of lead and releasing the acetic acid, which acts on a fresh portion of the plate, this action being repeated indefinitely until the desired thickness of oxidized coating is obtained. In the absence of an electric current this effect will take place but slowly, as the solution of the lead requires a continual decomposition of the water or of the acid to supply the necessary oxygen, resulting in the continual absorption of energy and in the evolution of hydrogen, which impedes the operation. By the electric current, however, the oxygen or acid radical is freed from the hydrogen, and the latter is set free at a point out of contact with the anode-plate. The formation therefore proceeds with great rapidity when thus assisted by the electrolytic action. A further effect of the electrolytic action is to deposit the oxidized material in more coherent contact with the plate, and the final result of such action is to peroxidize the said material.

I have shown at 7 in Fig. 1 a terminal plate serving as a cathode while the plate A is being formed. When such formation is completed, the terminal 7 is removed and the plate A is put in its place as a cathode, as indicated in Fig. 2, a new unformed pickled plate A' being placed in the bath as an anode. The electrolytic action then proceeds as before, resulting in the oxidation of plate A'.

At the same time the oxidized coating on the cathode-plate A is reduced by reason of the same electrolytic action, and in its reduction it causes oxidation of the hydrogen released by electrolytic action at the cathode, and thereby diminishes the amount of energy required to force the electric current through the bath. The bath contains no reducible substance—that is to say, no substance that is readily reduced by free hydrogen—so that the oxidation of the released hydrogen is not effected at the expense of the electrolyte, but by the action of the cathode alone. It is therefore essential that the solvent acid in the bath should not readily give up oxygen, a condition that is not compatible with the use of nitric acid as the solvent, but is fulfilled by many organic acids—such as acetic acid, formic acid, &c.—any one of which may be used in connection with a suitable precipitating acid, preferably sulfuric acid. Most of the mineral acids other than nitric form comparatively insoluble salts with lead and are therefore not suitable for use as solvents. The plate is thus exposed as a cathode to electrolytic action sufficiently to completely reduce it and at the same time free it to a great extent of the nitric sulfuric acetic salts that may have been retained therein from the previous treatment, as before explained. To this end the electrolytic action may be continued after the complete reduction of the oxidized plate and until hydrogen is freely evolved. A strong cleansing action is thus produced, and the plate is removed from the forming-bath with its surface coated with a deposit of porous or spongy lead. A final cleansing operation is preferably performed in a separate bath under electrolytic action, as set forth in the other divisional application to which I have already referred.

Having thus described my invention, the following is what I claim as new therein and desire to secure by Letters Patent:

1. The process of forming a lead storage-battery plate which consists in forming an oxidized coating on the plate by making it the anode in an electrolytic bath, the electrolyte of which produces an oxidizing chemical reaction upon the anode, whereby a continuous electrochemical effect takes place, and then shifting the plate thus provided with the oxidized coating into the position of cathode and introducing a new unoxidized plate as anode, whereby the reduction of oxid on the first-named plate serves to diminish the amount of energy required to oxidize the second plate.

2. The process of forming lead storage-battery plates which consists in exposing each a series of plates first as the anode and then as the cathode in an electrolytic bath containing sulfuric acid and a dissolving agent, whereby a continuous electrolytic action takes place without reversing the current, and each plate being exposed as an anode in association with a cathode comprising a preceding plate of the

series which has been exposed as an anode, substantially as and for the purpose set forth.

5 3. The process of forming lead storage-battery plates which consists in oxidizing a plate as an anode in an electrolytic bath, then shifting the plate thus oxidized into the position of cathode, then introducing a new plate as anode and oxidizing the latter in conjunction

with the previously-oxidized plate as cathode, the electrolyte being composed of acetic and 10 sulfuric acids.

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