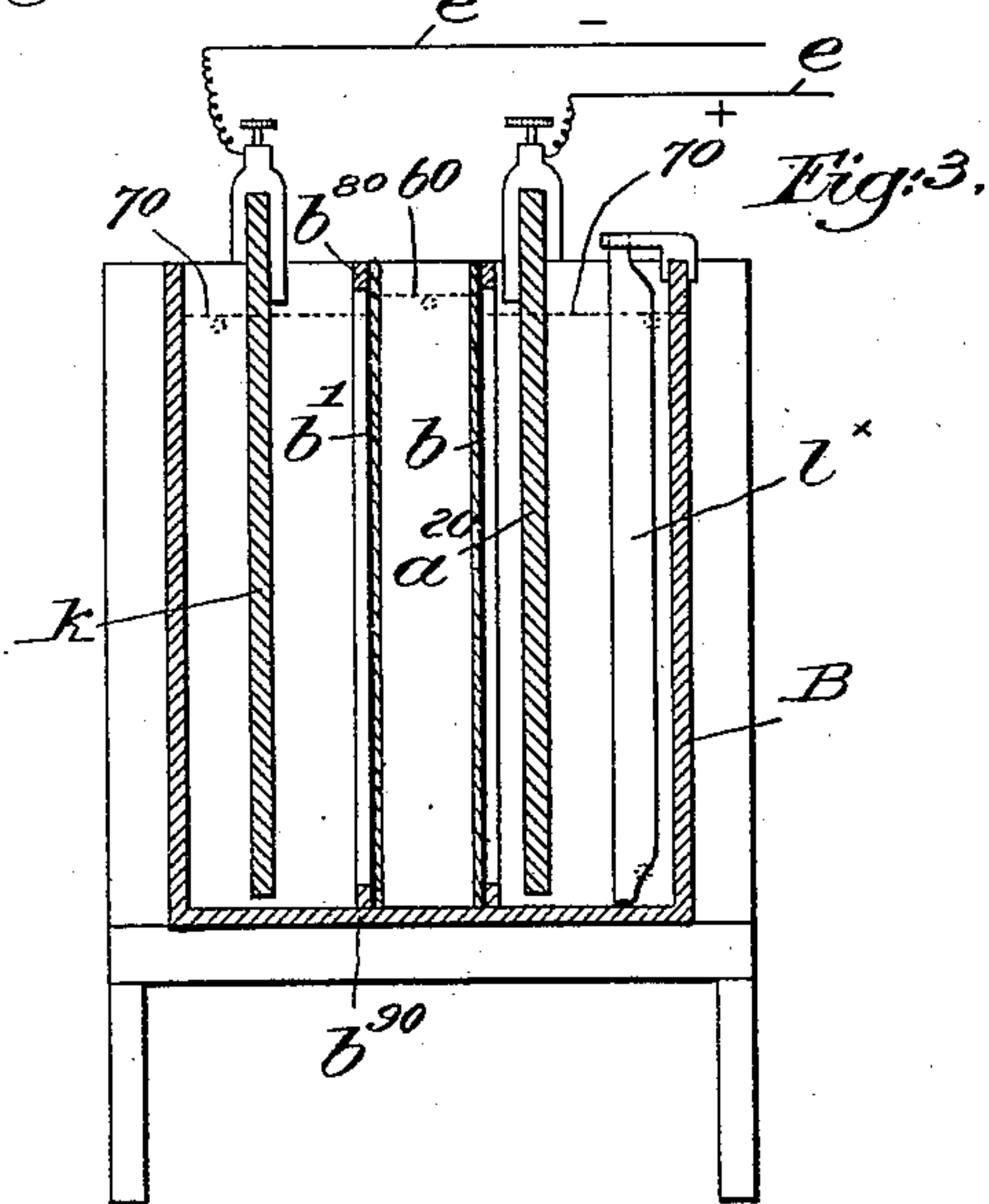
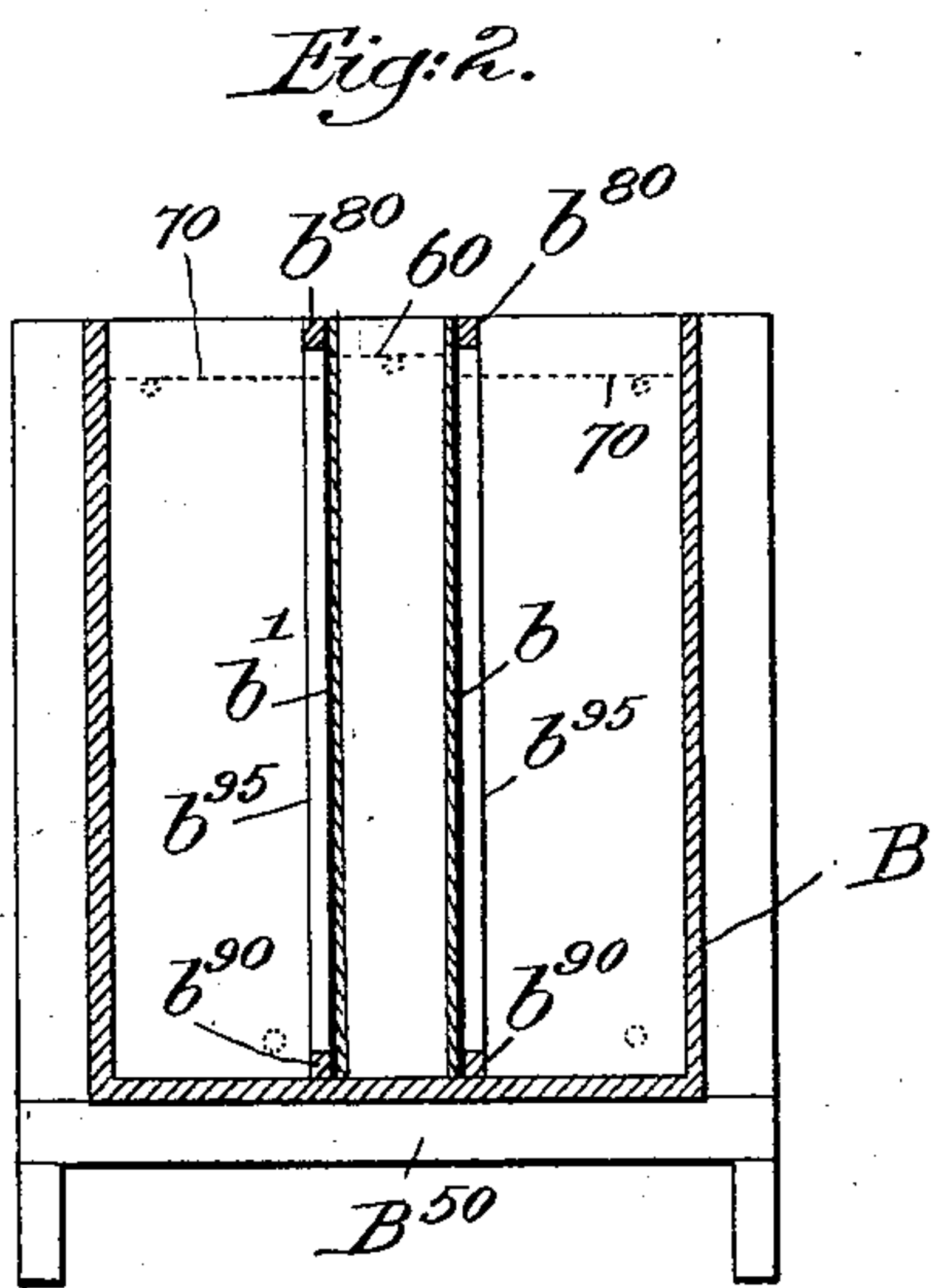
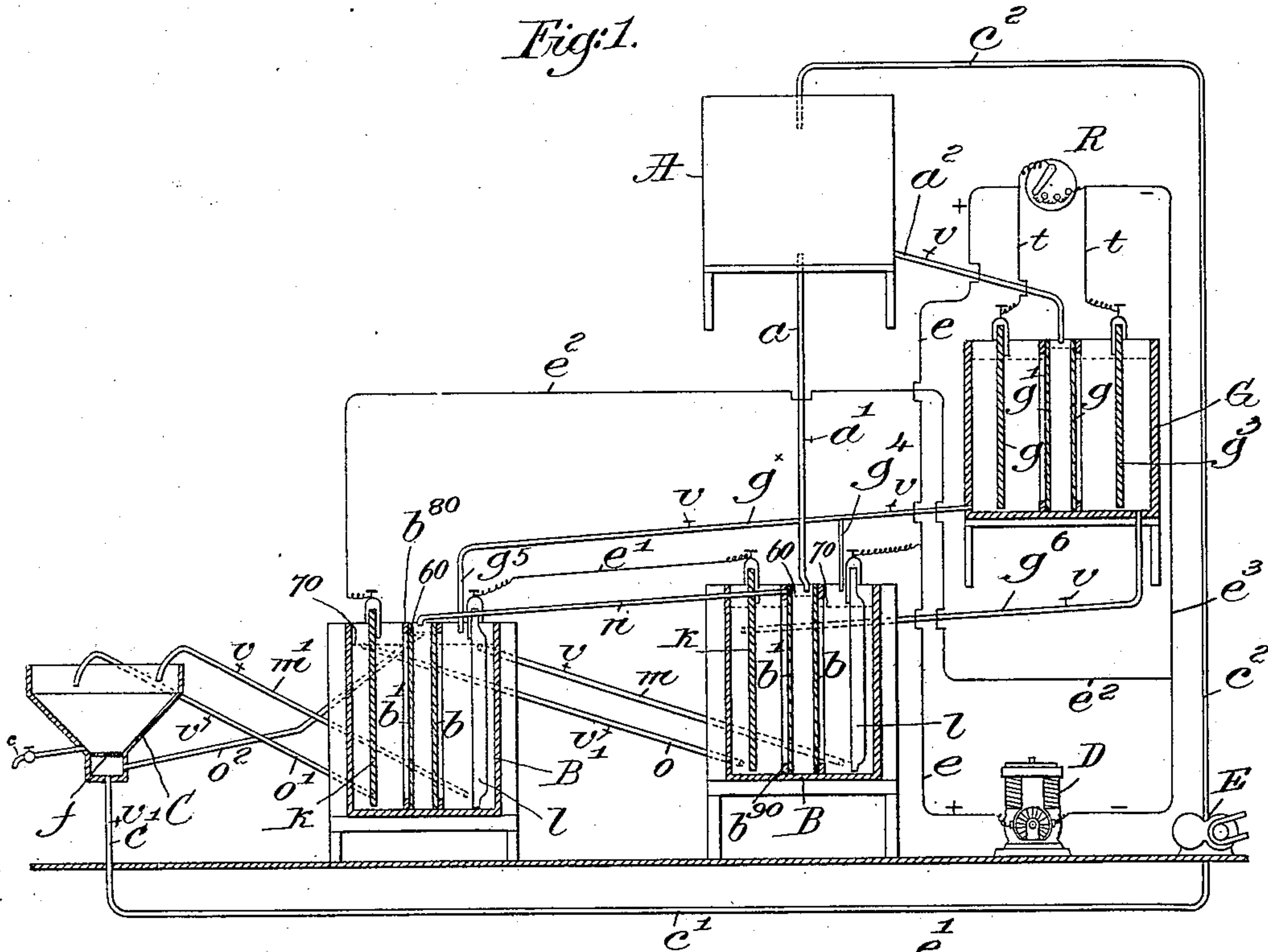


(No Model.)

A. B. BROWNE & E. D. CHAPLIN.
PROCESS OF MANUFACTURING WHITE LEAD.

No. 563,553.

Patented July 7, 1896.



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UNITED STATES PATENT OFFICE.

ARTHUR BENJ. BROWNE, OF CAMBRIDGE, AND EDWIN D. CHAPLIN, OF NATICK, MASSACHUSETTS, ASSIGNORS TO THE AMERICAN ELECTRIC LEAD COMPANY, OF KITTERY, MAINE.

PROCESS OF MANUFACTURING WHITE LEAD.

SPECIFICATION forming part of Letters Patent No. 563,553, dated July 7, 1896.

Application filed December 20, 1894. Serial No. 532,394. (No specimens.)

To all whom it may concern:

Be it known that we, ARTHUR BENJ. BROWNE, of Cambridge, and EDWIN D. CHAPLIN, of Natick, in the county of Middlesex, State of Massachusetts, have invented an Improvement in the Manufacture of White Lead, of which the following description, in connection with the accompanying drawings, is a specification, like letters on the drawings representing like parts.

In United States Patent No. 496,109, dated April 25, 1893, a process for making white lead is described, wherein a body of metallic lead to be acted upon is placed in an electrolytic solution, preferably a solution of a nitrate of an alkaline base, which, under the influence of an electric current, will separate into a solvent of lead at one pole and an alkaline hydrate at the other pole, and the solution is simultaneously electrolyzed by causing a current of electricity to flow from the metallic lead, which is therein described as the "anode," through said solution.

The solvent for lead separated at the anode dissolves said anode and forms a soluble salt of lead, while the alkaline hydrate accumulates at the cathode until disturbed by the flow of the solution to the said cathode, which disturbance causes the alkaline hydrate to mix with the soluble salt of lead, thereby forming and precipitating a hydrate of lead. The said precipitate settles and is subsequently removed and subjected to the action of carbonic-acid gas to form a hydrated carbonate of lead, the solution remaining after the removal of the lead hydrate being substantially in its original condition and fit to be used over again. This process while giving good results is objectionable, in that by reason of the complicated reactions which are set up the solution in the electrolyzer is rendered alkaline, resulting in the deposition of metallic lead on the cathode, thereby withdrawing an appreciable amount of metallic lead from the solution, and it is lost or becomes intermingled with and deteriorates the subsequently-precipitated hydrate of lead. A further objection to the said process resides in the fact that the lead hydrate is precipitated in the electrolyzer, from which it

must be removed during the operation of the process.

This invention has for its object the manufacture of white lead by a process which obviates the objections hereinbefore enumerated, the said process being hereinafter fully described in the specification and particularly pointed out in the claims.

Figure 1 of the drawings represents in vertical section and partially in diagram one form of apparatus adapted to carry out our invention. Fig. 2, on an enlarged scale, represents a sectional view of one of the tanks or electrolyzers; and Fig. 3, also on an enlarged scale, represents a tank for carrying out the process in a slightly-modified form.

We have shown the apparatus in Fig. 1 as composed of a supply-tank A, supposed to be supported above the rest of the apparatus in any suitable manner and having a discharge-pipe *a* leading therefrom and provided with a controlling-valve *a'* to control the flow through said discharge-pipe.

A tank or electrolyzer B is preferably arranged on a lower level than the supply-tank A and in a convenient position to receive the discharge therefrom by means of the pipe *a*. A second tank B', similar in construction to the tank B, is supported below it in order that liquid in the tank B may flow by gravity and through suitable pipes, to be described, into the tank B'.

The tanks themselves may be made of any suitable material not injuriously affected by the operation of the process to be described, each tank being supported on a suitable stand B⁵⁰, and we have divided each tank into three compartments by securing two diaphragms *b* and *b'* to preferably opposite ends of the tank in any suitable manner, and, as best shown in Fig. 2, bars *b*⁸⁰ and *b*⁹⁰ are attached to the ends of and extend across the tank, and to these bars the diaphragms are attached at their upper and lower edges, while upright cleats *b*⁹⁵ (shown only in Fig. 2) hold the vertical edges of the diaphragms against the tank ends, the diaphragms being represented by heavy black lines, said diaphragms permitting the passage therethrough of the electrolyte, and the diaphragms are hereinafter

designated as "foraminous," meaning by such term diaphragms of pervious or porous material, or of impervious material having small openings therein.

5 In carrying out our invention we prefer to use stout but light canvas or cloth.

We have discovered that the separation of an electrolyte into its anion and cation by the passage of an electric current therethrough
10 may be maintained indefinitely if a preponderance of pressure of the electrolyte is maintained on the inner sides of two foraminous diaphragms interposed between the poles in the electrolyte, and we have utilized this op-
15 eration in the manufacture of white lead.

While the simplest way now known to us of maintaining the preponderance of pressure on the inner sides of the diaphragms is by maintaining the level of the electrolyte
20 between the diaphragms higher than the level of the anion or cation liquid outside of said diaphragms, our invention is not restricted to such means for maintaining the required difference of pressure.

25 The diaphragms mark very clearly the divisions between the compartments containing the electrolyte and its separated components, but the difference of pressure referred to is the essential feature in maintaining the
30 components separated indefinitely.

By the term "electrolyte" we mean a liquid which will be separated by electrolysis into anion and cation, and in carrying out our process for making white lead we employ as
35 the electrolyte any liquid which will be separated by the passage of an electric current therethrough into a solvent for lead and an alkaline hydrate, such, for instance, as a solution of a nitrate, or an acetate, of an alkaline base. We prefer, however, to use a solution of a nitrate of an alkaline base, and the solution may be composed of any single salt or of a combination of two or more salts, provided the hereinbefore-mentioned separation by electrolysis takes place.
45

In the apparatus shown the spaces between the diaphragms in tanks B and B' are connected at their upper ends by a suitable pipe *n* to form an overflow for the electrolyte from
50 the first tank into the second tank.

The compartment outside of the diaphragm *b* in tank B is connected with the corresponding compartment in tank B' by a pipe *m*, and the compartment outside of the diaphragm
55 *b'* in tank B is connected with the corresponding compartment in tank B' by pipe *o*, the said pipes leading from, preferably, at or near the bottom of the first tank to the upper part of the second tank.

60 The compartments in the tank B' at the outer sides of the diaphragms *b* and *b'* are provided, respectively, with discharge-pipes *m'* and *o'*, which open into a mixing or settling tank or vessel C, arranged, preferably,
65 at a lower level than the tank B', the pipes *m*, *m'*, *o*, and *o'* being provided with suitable

valves *v* for regulating the flow of the liquids therethrough.

The bottom of the settling-tank C is preferably inclined toward the center and is provided with a filter *f*, of any suitable material,
70 located below a discharge-pipe *c*. The space below the filter *f* is connected by a pipe *c'* with a suitable pump E, the delivery-pipe *c''* of said pump leading to and opening into the
75 supply-tank A.

In carrying out our process the supply-tank A is charged with the electrolyte, preferably nitrate of soda dissolved in water, and the metallic lead to be acted upon is placed in
80 the anode-compartments of the tanks B B', and, as shown in Fig. 1, the lead itself, preferably in the form of pigs, as *l*, forms the anode for each tank.

The cathode *k*, which may be any conductor substantially insoluble in the cation, such as copper, is placed in the other compartment of each tank outside of the diaphragm *b'*, and the anode of the first tank is connected by wire *e* with the positive pole of the dynamo
85 D or other source of electrical power, and the corresponding cathode *k* is connected by wire *e'* to the anode *l* of the second tank, the cathode *k* of said latter tank being connected electrically with the negative pole of the dynamo
90 or other source of electrical power by a wire *e''*.
95

The valve *a'* being opened, and also the valves *v* in the various pipes, the electrolyte will be discharged into the first tank between the diaphragms *b b'*, and as the latter are
100 foraminous the fluid will pass therethrough, and an electric current is passed through the electrolyte from the anode to the cathode, care being taken, however, to maintain the pressure of the electrolyte upon the inner
105 sides of said diaphragms greater than the pressure upon the outer sides thereof, which is conveniently accomplished by maintaining the level of said electrolyte higher between the diaphragms than the level of the liquid
110 in the exterior compartments of each tank.

In the drawings the level of the fluid between the diaphragms is denoted by the dotted line 60, and the level of the fluid outside of the diaphragms by the dotted line 70.
115

The passage of the electric current through the electrolyte separates the latter into a solvent of lead in the compartment in which the anode is located and into an alkaline hydrate in the compartment containing the
120 cathode, and so long as the preponderance of pressure upon the inner sides of the diaphragms is maintained, the separation of the electrolyte into a solvent for lead and an alkaline hydrate will be maintained.
125

The solvent of lead or the anion so separated acts upon the metallic lead and forms a soluble salt of lead, and if a nitrate of an alkaline base is used as the electrolyte, lead nitrate will be formed thereby.
130

When the tank B is filled by the different fluids, that is to say, by the electrolyte be-

tween the diaphragms, and the solvent of lead in the anode-compartment and the alkaline hydrate in the cathode-compartment, up to the levels shown by broken lines 60 and 70, respectively, the electrolyte will overflow through pipe *n* into the compartment in the tank B' between the diaphragms *b b'*, and the anion and cation liquids will flow through the pipes *m* and *o*, respectively, into the "anode" and "cathode" compartments, as they may be called, of the tank B', and the separation of the electrolyte takes place in the latter tank as has been described as taking place in the tank B, the electrolyte in the second tank being decomposed by the passage of the electric current, with the separation and maintenance of the anion or solvent of lead in the anode-compartment and the cathion or an alkaline hydrate in the cathode-compartment, each mingling with the liquid which has been brought over from the corresponding compartment in the preceding tank.

It will be understood that as the operation is continuous fresh electrolyte will be practically continuously introduced into the first tank, and the surplus not required to maintain the requisite difference of level hereinbefore referred to will flow over to and supply the two compartments with fresh electrolyte, and so on, and the same is true of both the solvent for lead and the alkaline hydrate.

While only two tanks have been herein shown, as many may be employed as is desired or convenient, each tank being located preferably at a lower level than the preceding tank, in order that gravity may cause the flow of the liquids throughout the series, and it is equally obvious that the process might be carried out with only one tank, provided it be connected with the settling-tank, as is the tank B'.

The alkaline hydrate and the lead in solution are withdrawn from the last tank of the series through the pipes *o'* and *m'*, respectively, and discharged into the settling-tank C and there intermixed, the alkaline hydrate mixing with the soluble salt of lead and thereby precipitating a hydrate of lead, which will settle at the bottom of the tank upon the filter *f*, while the solution or filtrate will pass through the filter and into the pipe *c'*, the said filtrate being substantially the original electrolyte and fit to be used over again in the process.

The filtrate is transferred to the supply-tank A by means of the pump E and pipe *c*².

The hydrate of lead which is left in the settling-tank is withdrawn therefrom from time to time by or through the discharge-pipe *c*, and it is thereafter subjected to the action of carbonic-acid gas, either as in said United States Patent No. 496,109, hereinbefore referred to, or as in United States Patent No. 527,830, dated October 23, 1894, or the hydrate is treated with a solution of a carbonate of an alkaline base, as, for instance, a carbonate

of soda, to change the hydrate of lead into a hydrated carbonate of lead.

While we have herein shown the metallic lead as forming the anode, it is obvious that the anode may be entirely independent of the metallic lead, as shown in Fig. 3, wherein the anode *a*²⁰ may be carbon and connected to the positive wire *e*, the cathode *k* of copper being connected to wire *e'*, while the metallic lead *l*^x is placed in the anode-compartment. When, however, the metallic lead forms the anode, as shown in Fig. 1, subsequent action of the electric current will, if not modified, so affect the composition of the anion as to cause the formation of lead nitrite, hyp-nitrite, and basic nitrite, probably in the order named, and a deposition of a basic salt will form on the diaphragms and on the tank, and such formation would be changed by the action of the electric current into a compound of complicated structure, causing a diminution of the resultant product.

The addition to the solvent of lead of an oxidizing agent which has no injurious effect upon the resultant product will so modify the composition of the anion that such deleterious formation is entirely prevented, and in carrying out the process herein described the oxidizing agent used is nitric acid, which should be preferably added constantly to the solvent of lead.

If it is desirable for any reason to carry on the process without the constant addition of the nitric acid referred to, the crystals of basic lead salt may be permitted to form so long as they do not collect on the foraminous diaphragms, for subsequent addition of the requisite quantity of dilute nitric acid will dissolve the crystals.

Nitric acid may be conveniently generated in conjunction with the main process by providing a tank G, (see Fig. 1,) located, preferably, below the supply-tank A and above the electrolyzing-tank B, said tank G having two foraminous diaphragms *g g'* therein, and an anode *g*², of carbon, in one of the outer compartments, and a cathode *g*³, of copper, in the other compartment. Said anode and cathode are shown as arranged in multiple arc in circuit with the dynamo by shunt-wires *t t'*, connected to the wires *e* and *e*³, respectively, the shunt-circuit including a rheostat R, by which the current through the electrolyte in the tank G can be regulated.

The compartment between the diaphragms *g g'* receives the electrolyte from the supply-tank A through a pipe *a*², and the pressure of the electrolyte on the inner sides of the diaphragms is maintained greater than the pressure upon the outer sides thereof, while the passage of the electric current through the electrolyte causes its separation into alkaline hydrate on the cathode side of diaphragm *g'* and into nitric acid on the anode side of diaphragm *g*, it being supposed that the electrolyte used is a solution of a nitrate of an alkaline base. The acid thus generated is con-

veyed by pipe g^x and branches g^4 and g^5 to the compartment in each tank B B' containing the solvent of lead, while the alkaline hydrate is conveyed by pipe g^6 to the compartment of the first tank containing the alkaline hydrate separated in said tank.

The various pipes are provided with suitable valves v to regulate or cut off altogether the flow of fluid therethrough, according to circumstances. It is to be understood, however, that the acid may be added to the solvent of lead in the electrolyzing tank or tanks in any other convenient manner, if desired, without departing from the spirit and scope of our invention.

By the herein-described process, which is a continuous one, we are enabled to produce from pure metallic lead a hydrate of lead of great purity in an expeditious and cheap manner, free from the admixture of impurities, whether in the form of blue lead or crystals of a substantially insoluble lead salt.

While the apparatus herein shown is well adapted for carrying out our process, it is obvious that the process may be carried out by other means, and our invention is not restricted to any particular form of apparatus.

We claim—

1. The herein-described process in the manufacture of white lead by the separation of an electrolyte into a solvent of lead and an alkaline hydrate, which consists in passing an electric current from anode to cathode through the electrolyte and two foraminous diaphragms therein between the anode and cathode, to separate said electrolyte into a solvent of lead and an alkaline hydrate; maintaining the solvent and the hydrate separated on the outer sides of the diaphragms by preponderance of pressure of the electrolyte on the inner sides of the diaphragms; subjecting the metallic lead to the action of the solvent therefor, to form a soluble salt of lead; adding an oxidizing agent to the solvent of lead to prevent the formation of insoluble salts of lead; and withdrawing and

thereafter mixing the soluble salt of lead formed and the alkaline hydrate, to form a hydrate of lead, substantially as described.

2. The herein-described process in the manufacture of white lead by the separation of an electrolyte into a solvent of lead and an alkaline hydrate, which consists in passing an electric current from anode to cathode through the electrolyte and, a separating foraminous diaphragm between the anode and cathode, to separate said electrolyte into a solvent of lead and an alkaline hydrate; subjecting metallic lead to the action of the solvent therefor, to form a soluble salt of lead; adding an oxidizing agent to prevent the formation of insoluble salts of lead, withdrawing and mixing the soluble salt of lead formed and the alkaline hydrate, to form a hydrate of lead; and finally carbonating said lead hydrate, substantially as described.

3. The herein-described process in the manufacture of white lead by the electrolytic separation of an electrolyte into a solvent of lead and an alkaline hydrate, which consists in passing an electric current from anode to cathode through the electrolyte and a separating foraminous diaphragm between the anode and cathode, to separate said electrolyte into a solvent of lead, an alkaline hydrate; subjecting metallic lead to the action of the solvent therefor, to form a soluble salt of lead; adding an oxidizing agent to the solvent of lead to prevent the formation of insoluble salts of lead; and withdrawing and mixing the soluble salt of lead formed and the alkaline hydrate, to form a hydrate of lead, substantially as described.

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

ARTHUR BENJ. BROWNE.
EDWIN D. CHAPLIN.

Witnesses:

JOHN C. EDWARDS,
AUGUSTA E. DEAN.