(No Model.)

A. B. BROWNE.

MANUFACTURE OF WHITE LEAD.

No. 563,555. Patented July 7, 1896.

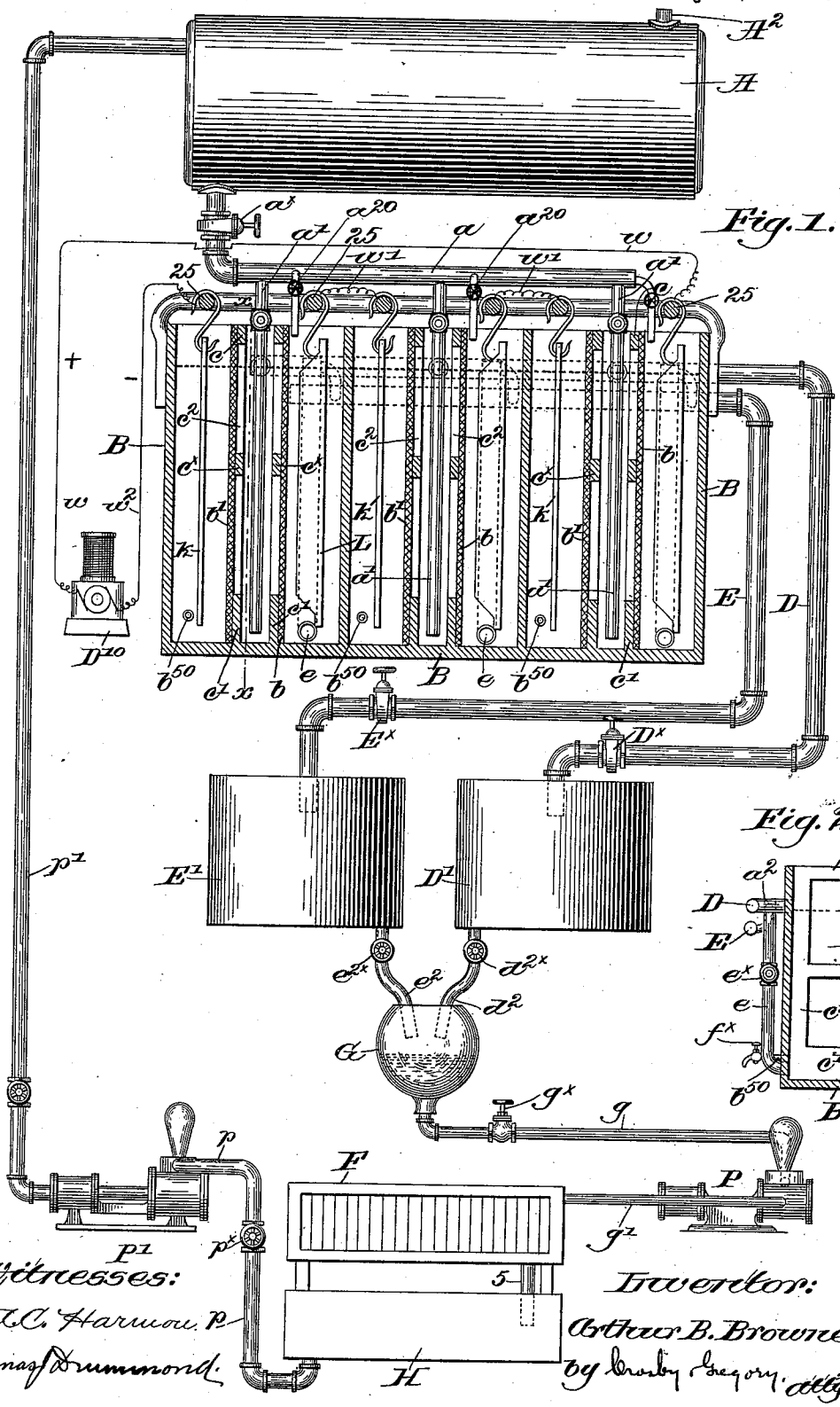

Fig. 1.

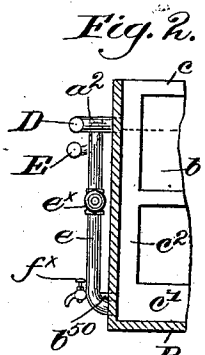

Fig. 2.

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UNITED STATES PATENT OFFICE.

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MANUFACTURE OF WHITE LEAD.

SPECIFICATION forming part of Letters Patent No. 563,555, dated July 7, 1896.

Application filed April 3, 1896. Serial No. 586,031. (No specimens.)

To all whom it may concern:

Be it known that I, ARTHUR BENJ. BROWNE, of Boston, county of Suffolk, 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.

This invention relates to the manufacture of white lead electrolytically, wherein metallic lead is acted upon by a solvent separated from an electrolyte by passage of an electric current therethrough, the metallic lead being converted by the solvent to a soluble salt of lead and thereafter mixed with or subjected to the action of an alkaline hydrate separated by the electrolysis from the electrolyte, resulting in a precipitation of a hydrate of lead. The hydrate of lead is thereafter carbonated in any suitable manner, forming a hydrated carbonate of lead, and the solution remaining after the precipitation is in substantially its original condition and fit to be used again as the electrolyte.

In another application, Serial No. 532,394, filed jointly by me and Edwin D. Chaplin, an improved process was described wherein the electric current passed through the electrolyte and two foraminous diaphragms interposed between the anode and cathode, the separation of a solvent of lead and an alkaline hydrate by the electrolysis being maintained on the outer sides of the diaphragms by a preponderance of pressure of the electrolyte on the inner sides of the diaphragms. The metallic lead in such process preferably formed the anode, and in practice it was found that the action of the electric current, if unmodified, would cause the deposition of a basic salt on the diaphragms and electrolyzer, which deposit would be changed by the action of the current into a compound of complicated structure, causing a diminution of the resultant product. Not only this, but there was also found to be a loss of soda, the electrolyte used being a solution of nitrate of soda, probably in accordance with the following equation:

$$\text{I.}\quad \begin{cases} 3Pb+8NaNO_3+4H_2O=\overset{-}{3Pb(NO_3)_2}+\overset{+}{2NO}+\overset{+}{8NaOH} \\ 3Pb(NO_3)_2+8NaOH=3PbO_2H_2+2NaOH+6NaNO_3, \end{cases}$$

it being obvious therefrom that of every eight molecules of $NaNO_3$ used in the process at the beginning only six molecules thereof were recovered, and that an excess of two molecules of NaOH remained out of every eight molecules of $NaNO_3$ in solution at the beginning. An oxidizing agent was added extraneously in conducting such process, and the reactions may be expressed as follows, it being remembered that the reactions expressed in the right hand of the first equation and on the left-hand side of the second equation were occurring at the same time:

$$\text{II.}\quad \begin{cases} Pb+O+2NaNO_3+2H_2O=\overset{-}{Pb(NO_3)_2}+\overset{+}{2NaOH}+H_2O \\ Pb(NO_3)_2+2NaOH=PbO_2H_2+2NaNO_3, \end{cases}$$

showing no loss of sodium nitrate and consequently no excess of alkali. Equation II thus shows how the result of the reaction expressed by equation I may be corrected by the extraneous addition of an oxidizing agent, but in my efforts to obviate such addition I have discovered a process, forming the subject-matter of this application, which renders entirely unnecessary extraneous addition of an oxidizing agent, the formation of subsalts of lead in my present process being prevented by maintaining the solution in the anode-compartment at a given density, preferably by adding fresh nitrate solution and withdrawing the soluble lead salt as necessary.

My invention is hereinafter fully described in the specification and particularly pointed out in the claims.

Figure 1 of the drawings represents in elevation and partially in section one form of apparatus adapted to carry out my invention, the electric circuit being shown diagrammatically; and Fig. 2 is a partial transverse sectional view, on a smaller scale, of one of the electrolyzers, taken on the line $x\ x$, Fig. 1.

For greater convenience of operation I have shown the main parts of the apparatus arranged on three different levels, utilizing gravity largely in transferring the different liquids from one portion of the apparatus to another, a supply-tank A being supported in any suitable manner at the highest point and having a discharge-pipe a, provided with a controlling-valve $a^{\times}$. One or more tanks or electrolyzers B are arranged on a lower level than the supply-tank, three electrolyzers being shown in Fig. 1, said tanks being made of any suitable material not injuriously af-

fected by the operation of the process. Each tank B is divided into three compartments by securing two diaphragms b and b' to cross-bars c c', extending across the electrolyzer at top and bottom, the sides of the diaphragms being secured to strips or cleats c^2 on the tank ends, an intermediate cross-bar $c^\times$ being sometimes used if the tanks are large. The diaphragms are pervious to permit the passage or percolation of the electrolyte therethrough, and stout canvas or cloth, or what is known as "asbestos millboard," may be used for the diaphragms.

In carrying out my process I prefer to use as the electrolyte a solution of a nitrate of an alkaline base, although it may be any liquid which will be electrolytically separated into a solvent for lead and an alkaline hydrate, such, for instance, as a solution of an acetate of an alkaline base.

Referring to Fig. 1, an inlet-pipe a' leads from the main discharge a of the supply-tank A to near the bottom of the space between the diaphragms b and b' in each electrolyzer B, while from near the upper end of each of such spaces an outlet-pipe a^2 leads to a common outlet D, said inlets and outlets having suitable controlling-valves 1 and 2 therein, respectively. A pipe e, open at its lower end, leads from at or near the bottom of the compartment outside the diaphragm b of each tank B up and out into a pipe E, from which the liquid contents of said compartments are drawn, said pipe E leading to a tank E', and pipe D to a tank D', both preferably below the electrolyzers, to avoid pumping. Valves $e^\times$ are located in the pipes e, and valves $D^\times$ and $E^\times$ in the pipes D and E, respectively, so that control of the contents may be had at all times.

The compartments at the outer side of the diaphragms b' are preferably provided each with an outlet b^{50} and stop-cocks $f^\times$, (see dotted lines Fig. 1,) so that the contents may be partly or wholly withdrawn when desired, it being obvious from the foregoing, however, that each electrolyzer is independent of its fellows. The outlets d^2 e^2 of tanks D' and E', having valves $d^{2\times}$ $e^{2\times}$, respectively, discharge into a common receptacle G, herein shown as substantially spherical and preferably made of glass, in order that the contents may be readily examined at any time. A discharge-pipe g from the vessel G, having a valve $g^\times$, forms the inlet of a suitable pump P, the outlet g' thereof leading to a filter-press F, of any well-known construction, said press having an outlet 5, opening into a tank H. The tank H has a discharge-pipe p, provided with a valve $p^\times$, leading to and forming the inlet of a second force-pump P', the outlet p' of said pump leading, as shown in Fig. 1, to the supply-tank A, so that the contents of the tank H can be pumped up thereinto, the supply-tank having a suitable vent A^2.

The supply-tank A is charged with the electrolyte, preferably nitrate of soda dissolved in water, and passes therefrom through pipes a and a' to the electrolyzers B, entering each at the bottom of the space between the two diaphragms, the metallic lead to be acted upon being herein shown as forming the anode for each tank, and in the form of pigs L it is placed in the anode-compartments.

The cathode k, any conductor substantially insoluble in the electrolyte, such, for instance, as copper, is placed in the compartment of each tank B outside of the diaphragm b', the anodes and cathodes being suspended from insulated supports 25, the anode of the first tank being connected by wire w with the positive pole of a dynamo D^{10} or other source of electrical power, while the corresponding cathode k is connected by wire w' to the anode L of the next tank, and so on throughout the series, the cathode k of the last tank B being connected by a wire w^2 with the negative pole of the source of electrical power. The proper valves being opened, the electrolyte will be discharged into the tanks B between the diaphragms, and as the latter are pervious the liquid will pass therethrough, and the electric current is passed through the electrolyte, separating it into a solvent of lead at the anode and an alkaline hydrate at the cathode, the solvent of lead or the anion acting upon the metallic lead to form a soluble salt of lead, lead nitrate if a nitrate of an alkaline-base is the electrolyte.

I have found in practice that percolation of the alkaline hydrate solution through the diaphragm into the anode-compartment will occur when a certain density or strength of such solution is attained, and in order to maintain the separation of the solvent of lead I keep the density of the solution between the diaphragms below such "critical point," as it may be termed, by withdrawing the solution, as it becomes alkaline, through the outlets a^2, taking its place with fresh electrolyte introduced between the diaphragms by the pipes a'.

Inasmuch as the solution between the diaphragms becomes more strongly alkaline toward the upper part of the compartment, I prefer to withdraw therefrom, and to introduce the fresh electrolyte near the bottom of the compartment, as shown. The withdrawn alkaline hydrate solution flows through pipe D into the tank D', and the lead in solution is withdrawn by the pipes e into the pipe E and thence to tank E'. The contents of tanks D and E are drawn off into the receptacle G and intermixed, the alkaline hydrate mixing with the soluble salt of lead and precipitating a hydrate of lead, which is forced by the pump P into the filter-press F, wherein the hydrate of lead is retained, the solution or filtrate passing into the vessel H substantially the original electrolyte, and fit to be used over again in the process. It is pumped back into the supply-tank A by the pump P'. The hydrate of lead left in the filter-press is with-

drawn at the proper time and carbonated in any suitable manner to change the hydrate of lead into a hydrated carbonate of lead.

In carrying out the process as thus described I have found that the metallic lead becomes oxidized on its surface, the coating of oxid eventually attaining a considerable depth, and I deduce therefrom the following equation:

III. $$\begin{cases} Pb+3H_2O+2NaNO_3=PbO+2NaNO_3+2H_2O+2H \\ PbO+2NaNO_3+2H_2O+2H=\overbrace{Pb(NO_3)_2}^{-}+\overbrace{2NaOH+H_2O+2H}^{+} \\ Pb(NO_3)_2+2NaOH=PbO_2H_2+2NaNO_3, \end{cases}$$

showing the production of a lead hydrate without its equivalent of alkaline hydrate, as distinguished from equation I and without the extraneous addition of an oxidizing agent.

I have found that a current density of 0.1 ampere per square inch is well adapted for use in carrying out the process.

The liquid in the compartment outside of the diaphragm b' of each electrolyzer becomes a very strong alkaline hydrate, and, if necessary, it may be used to increase the alkaline condition of the liquid withdrawn from between the diaphragms, as hereinbefore described, the cathode-compartments being provided with suitable outlets b^{50}.

The apparatus herein shown is well adapted for carrying out the process effectively and economically, but it is obvious that the process may be carried out by other means, and that by using suitable pumps the whole apparatus may be located on one floor of a building.

To prevent the formation of subsalts of lead in the anode-compartments, I maintain the solution therein at a substantially uniform density by introducing fresh electrolyte through suitable pipes a^{20}, Fig. 1, and withdrawing the soluble salt of lead formed through the outlets *e*.

Having fully described my invention, what I claim, and desire to secure by Letters Patent, is—

1. In the manufacture of white lead by electrolysis, introducing the electrolyte between two pervious diaphragms interposed between the anode and cathode, withdrawing the liquid from between the diaphragms as it becomes alkaline, subjecting metallic lead to the solvent of lead separated by passage of the current, to form a soluble salt of lead, and finally withdrawing said salt of lead and mixing it with the withdrawn alkaline liquid, to form a hydrate of lead, substantially as described.

2. In the manufacture of white lead by electrolysis, introducing the electrolyte between two pervious diaphragms interposed between the metallic lead anode and the cathode, withdrawing the liquid from between said diaphragms as it becomes alkaline, to prevent percolation of alkaline hydrate into the solvent of lead separated by passage of the current, withdrawing the soluble salt of lead formed by action of the solvent on the metallic lead, and mixing it with the withdrawn alkaline liquid to form a hydrate of lead, substantially as described.

3. In the manufacture of white lead by electrolysis, passing an electric current through the electrolyte and two pervious diaphragms between the anode and cathode, introducing fresh electrolyte between the diaphragms, the action of the current separating from the electrolyte a solvent of lead on the anode side of the diaphragms and an alkaline hydrate on the cathode side, withdrawing the liquid from between the diaphragms as it becomes alkaline, adding thereto alkaline hydrate from the cathode side of the diaphragms, subjecting metallic lead to the action of the solvent therefor to form a soluble salt of lead, and finally mixing the said salt of lead and the withdrawn strongly-alkaline liquid, to form a hydrate of lead, substantially as described.

4. In the manufacture of white lead by electrolysis, introducing the electrolyte between two pervious diaphragms interposed between the anode and cathode, withdrawing the liquid from between said diaphragms as it becomes alkaline, to thereby prevent percolation of alkaline hydrate into the solvent of lead in the anode-compartment separated by passage of the current, subjecting metallic lead to the action of the solvent, to form a soluble salt of lead, and maintaining the solution in the anode-compartment at a given density by adding fresh electrolyte and withdrawing the soluble lead salt, to prevent the formation of subsalts of lead, substantially as described.

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

ARTHUR BENJ. BROWNE.

Witnesses:
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JOHN C. EDWARDS.