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H. S. BLACKMORE.
PROCESS OF PRODUCING CAUSTIC ALKALI.
APPLICATION FILED MAY 10, 1905.

Fig. 1.

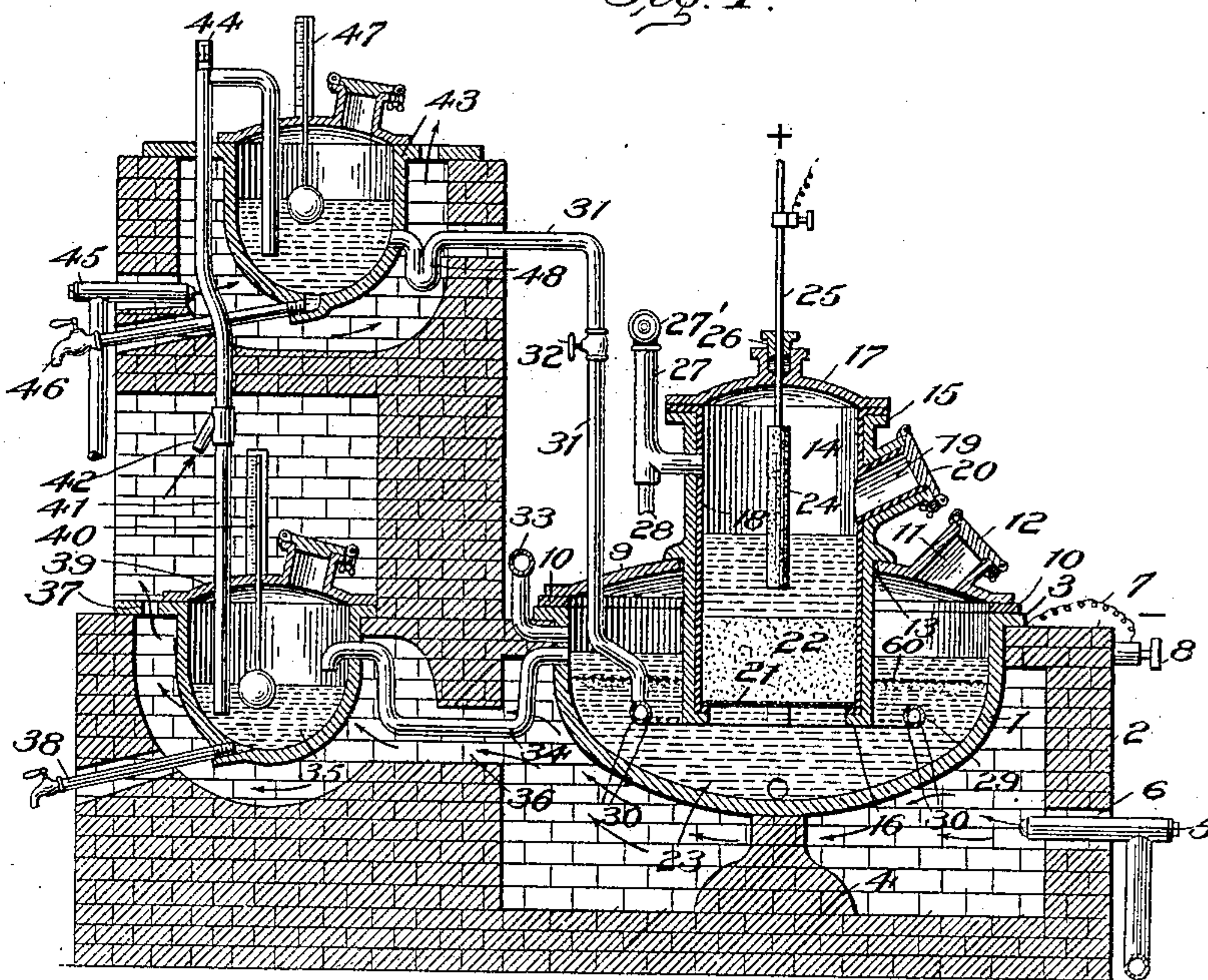


Fig. 3.

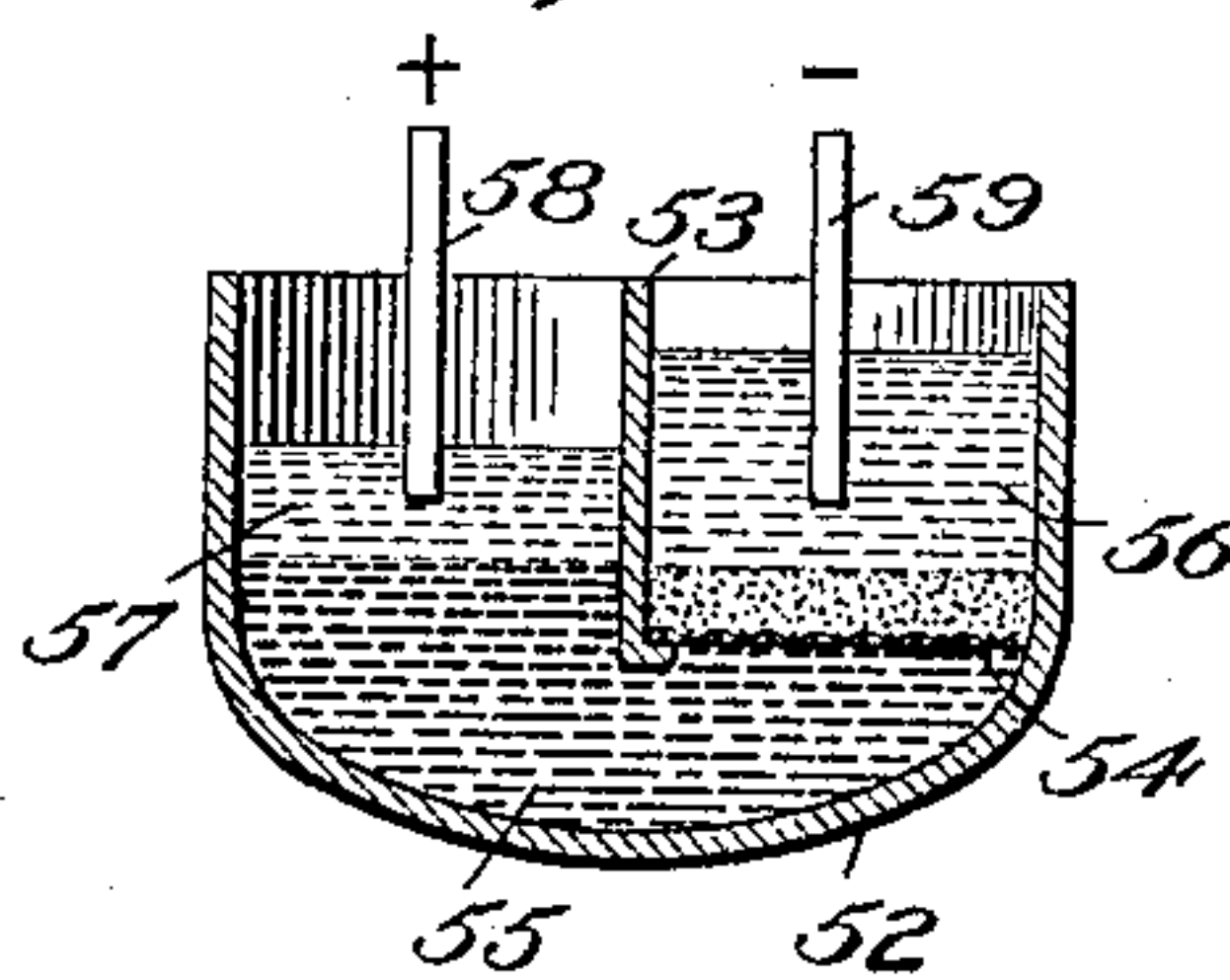
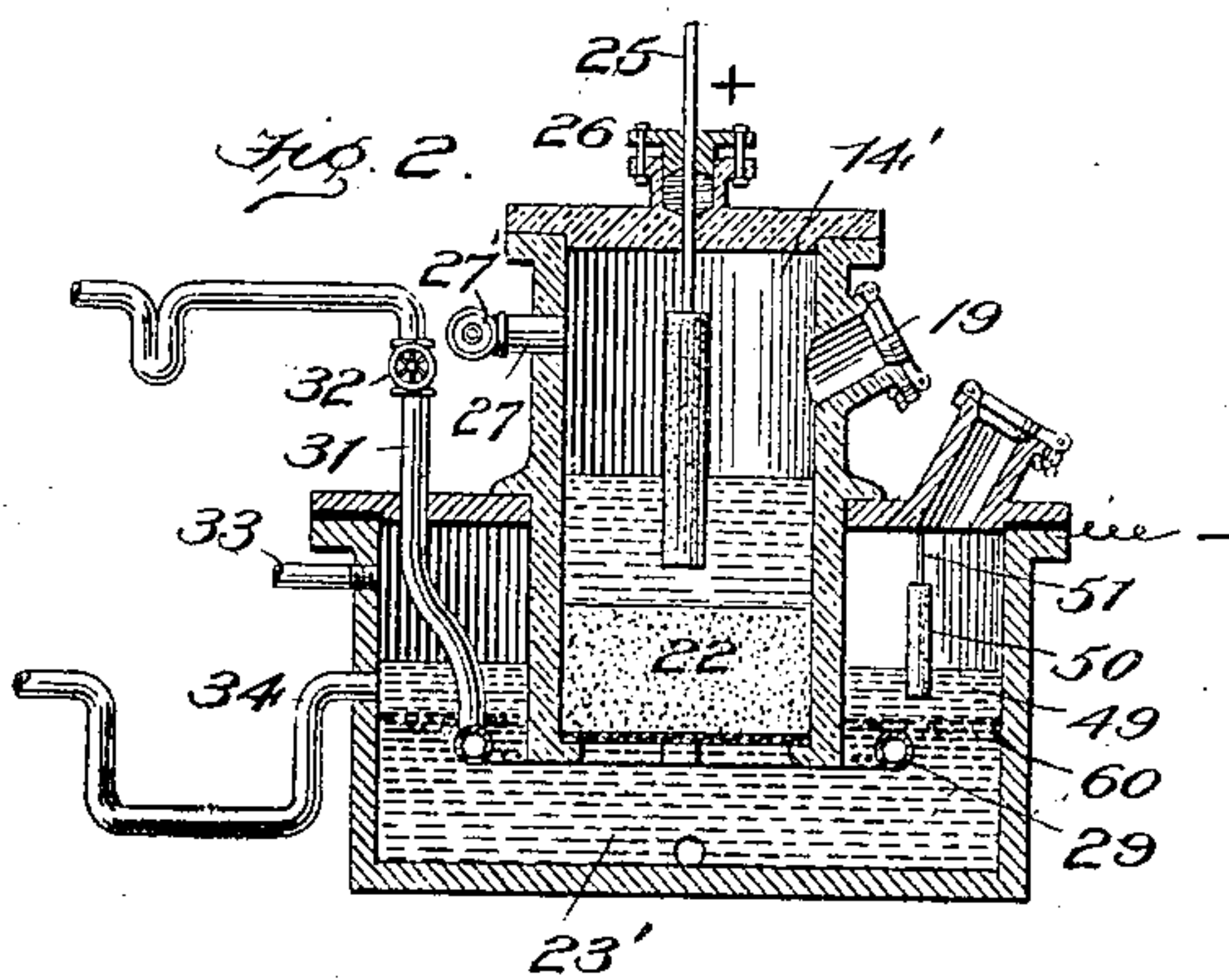


Fig. 2.



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PROCESS OF PRODUCING CAUSTIC ALKALI.

No. 809,088.

Specification of Letters Patent.

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Application filed May 10, 1905. Serial No. 259,818.

To all whom it may concern:

Be it known that I, HENRY SPENCER BLACKMORE, a citizen of the United States, residing at Mount Vernon, in the county of Westchester and State of New York, have invented certain new and useful Improvements in Processes of Producing Caustic Alkali, of which the following is a specification.

The object of my invention is to produce caustic alkali by electrolytic action in such a manner as to effect a saving in time and expense, together with a larger yield with less power in an automatic manner than has been obtained hitherto; and it consists of certain new and novel features, as hereinafter set forth.

My invention relates particularly to the production of caustic soda and chlorin from liquid or liquefied common salt, (sodium chlorid,) but is not limited thereto, as it may be applied to the production of many other alkalis, such as potassa or lithia, and other salts or compounds of alkali metals than the chlorid, such as sodium chlorid, as employed in the specific example of my process herein set forth.

In carrying out my invention for the production of caustic soda from liquid or liquefied sodium chlorid I proceed as follows, reference being had to the accompanying drawings, in which—

Figure 1 is a transverse vertical section of an apparatus employing a molten electrolyte and cathode. Fig. 2 is a transverse vertical section of an apparatus employing an aqueous solution of an electrolyte and a cathode of mercury, and Fig. 3 is a transverse vertical section of a modified apparatus.

The apparatus of Fig. 1 consists of the following parts: An iron vessel 1 is set within a furnace-casing 2, of fire-brick, and supported therein in part by an annular flange 3, extending outwardly from the upper edge of the vessel and resting upon the fire-brick, and in part by pier 4, rising centrally from the bottom of the furnace-chamber into supporting contact with the bottom of the vessel. The contents of the vessel are brought into a molten condition by any suitable means, that shown being a burner 5, extending through an opening 6 in the side wall of the furnace. The electrolyte and cathode may be subsequently maintained in a molten condition by the electrolyzing-current. From the flange 55 of the vessel a cathode-terminal 7 extends to a binding-post 8. The vessel has an iron cover

9, supported by, but insulated from, the vessel by an insulating packing 10, preferably of magnesia. The cover has a side opening 11, with closure 12 to permit the introduction of lead and a large central opening 13, within which is arranged the anode-chamber 14. This anode-chamber consists of a tubular casing 15, of iron, having an inwardly-extending flange 16 at its lower open end, a cover 17 with central opening for the anode-terminal, and a non-conducting lining 18, preferably of magnesia, which at the upper end of the chamber extends out between a flange at the upper end of the casing and a corresponding flange on the cover to provide an insulating-packing. The anode-chamber has a lateral neck 19, with tight-fitting cover 20, for the introduction of sodium chlorid or other material to be electrolyzed. The flange 16 at the lower end of the anode-chamber supports a disk 21, of foraminous material, preferably iron-wire gauze, which disk is overlaid by a diaphragm 22. This diaphragm preferably consists of loose granular material of greater specific gravity than the molten electrolyte and less specific gravity than the molten cathode arranged upon support 21 in a layer of considerable depth. The material which I have found especially suitable for such diaphragm when molten sodium chlorid is to be electrolyzed is magnetite broken into angular fragments of such size as to pass through a sieve having a mesh of fifty to the inch. The molten lead 23, acting as a cathode, preferably rises to such a height in vessel 1 that the entire mass of loose material 22 constituting the diaphragm floats upon the surface of the lead, the diaphragm thereby remaining in close contact with the cathode, notwithstanding considerable change in the surface-level of the molten lead. The wire-gauze 21 is merely a safety device to prevent the material of the diaphragm from dropping out of the anode-chamber in case the molten lead falls to any abnormal low level and is not necessary to the proper working of the apparatus. The anode 24, which may be a rod or rods of graphitized carbon, is carried by an adjustable rod 25, which may be of metal protected with porcelain, and extends through a stuffing-box 26 in cover 17. From one side of the anode-chamber extends an outlet-pipe 27 to draw off chlorin or other gaseous products, the removal of this chlorin being perfectly assisted by the action of an air-injector 28 in pipe 27, which serves to maintain

a slight vacuum in the anode-chamber. The lead-sodium alloy produced by electrolysis of the molten sodium chlorid being lighter than the lead is continuously displaced as formed from the surface of the cathode beneath the diaphragm and rises to the surface of the cathode around the anode-chamber, this being at a higher level than below the diaphragm. The alloy may be thence drawn off. It is preferable, however, to continuously remove the sodium from the alloy and convert it into its hydrate or oxid, the remaining lead being returned by gravity to the bottom of vessel 1 beneath the diaphragm to receive further additions of sodium. This result may be accomplished in various ways, but preferably by the following means: Within and some distance below the surface of the molten-lead cathode is an annular pipe 29 arranged around and concentric with the anode-chamber. This pipe has two rows of downwardly and outwardly opening perforations 30. Connecting with pipe 29 is a pipe 31, having valve 32, which serves for the introduction of molten sodium hydrate. This sodium hydrate, injected in a plurality of fine streams into the molten lead-sodium alloy, is reduced by the sodium to sodium oxid with evolution of hydrogen, which rises and passes off from the electrolytic cell through pipe 33. Sodium oxid rises and floats on the surface of the cathode and remaining in a molten condition is continuously drawn off as it rises above a certain level by an inverted siphon 34, extending from the side of vessel 1 and delivering into a vessel 35, situated in an adjoining chamber in the brickwork of the furnace. To facilitate the oxidation of the sodium, a layer 60 of loose granular conducting material is arranged at or near the surface of the cathode around the anode-chamber. This material may consist of small angular fragments of iron, magnetite, or ferrosilicon. The material should be, at least in part, beneath the surface of the cathode, and this arrangement may be effected either by employing a floating layer of such depth that its weight causes the lower particles to be submerged or by fixing a horizontal ring of wire-gauze between the anode-chamber 13 and the outer wall of the vessel at or below the surface of the cathode. This loose granular material serves to distribute the streams of sodium hydrate rising from pipe 29 and bring them into thorough and intimate contact with the sodium in the alloy. The oxidizing reaction is facilitated by the innumerable local couples due to the contact of the sodium and the relatively negative particles of iron, &c. The sharp corners of the particles also increase the speed of the reaction. The oxidation of the sodium may also be effected by successively introducing oxygen and hydrogen or air and natural gas through pipe 29, the oxygen serving to convert the lead-sodium alloy into sodium plumbate, which

is then reduced to metallic lead by the hydrogen with production of sodium hydrate.

The sodium oxid received in vessel 35 is maintained in a molten condition by any suitable means, as by the waste products escaping from the main furnace-chamber through a side passage 36, sweeping around the vessel and passing out through openings 37 in the supporting-flange of the vessel. Vessel 35 has a cover 39, through which passes the stem of a float level-indicator 40. The sodium oxid may be withdrawn, if desired, through valved outlet 38. It is preferred, however, to continuously convert this oxid into hydrate. For this purpose a pipe 41 leads upward from beneath the level of the molten oxid in vessel 35 past a steam-injector 42, which serves both to introduce the water necessary for hydration and to carry the old material upward to a vessel 43. The upper end of pipe 41 is bent and extends downward into vessel 43 to open beneath the surface of the molten sodium hydrate therein. A spring-closed air-inlet valve is arranged in the bend to prevent any siphoning of hydrate back through pipe 41. Vessel 43 is heated by a burner 45 and has a valved outlet 46 for the finished product. The cover of vessel 43 also carries a level-indicator 47. Such amount of sodium hydrate as is required to oxidize the sodium taken up by the lead cathode continuously passes off from vessel 43 through a trapped outlet 48, communicating with pipe 31.

The modification shown in Fig. 2 is similar in most respects to the apparatus already described, with the exception that a mercury cathode is employed, while the electrolyte is an aqueous solution, no external heat being therefore required. The anode-chamber 14' is preferably constructed of glass or porcelain without lining. The oxidation of the sodium taken up by the cathode 23' may be effected in the usual manner by placing a layer of water 49 on the surface of the cathode around the anode-chamber, into which depend carbon electrodes 50, short-circuited to the cathode by connections 51 to the metallic cover of the metal-containing vessel. We preferably employ, however, for this purpose a perforated annulus of pipe 29, like that heretofore described, by which water or a dilute solution of sodium hydrate is injected into the body of the mercury-sodium amalgam, the resulting strong-sodium-hydrate solution being withdrawn through side outlet 34. The resulting solution may be further strengthened by recirculating it through the amalgam with or without previous additions of water. The floating diaphragm 22 employed in this modification may be of broken magnetite, as heretofore, or of broken glass or silica sand. A layer 60 of conducting particles on and beneath the surface of the cathode around the anode-chamber may be employed to facilitate oxidation of the sodium, as here-

tofore described. When sodium or other easily-oxidizable metal is deposited into the mercury, the resulting amalgam being lighter than the mercury rises around the anode-chamber to a level where the sodium is oxidized and removed, the depleted mercury again returning to its position beneath the diaphragm.

The term "alloy" as used in the claims is intended to also cover an amalgam or alloy containing mercury.

Various modifications may be made in the apparatus shown and described within the scope of the generic claims. The partition which divides the containing vessel into an electrolyzing and an oxidizing compartment may be of other form and arrangement than the tubular anode-chamber shown. The diaphragm and superposed electrolyte may be placed outside of the tubular partition and the oxidizing agent introduced within it, or a straight depending partition may be employed to partially separate the two chambers.

By the term "depending partition" as used in the claims is meant any partition which has a passage or passages at its lower portion. If the diaphragm is a rigid sheet, both it and the partition may be arranged in an inclined position. In some cases the diaphragm may be entirely omitted if care is taken to maintain the bodies of electrolyte, liquid metal, and products of oxidation at uniform levels.

The height of the column of electrolyte required to counterbalance the liquid-metal cathode outside the anode-chamber may be decreased by slightly increasing the normal atmospheric pressure on the surface of the electrolyte. This may be easily effected by restricting the outflow of chlorin by regulating valve or choking device 27' in the outlet-pipe 27 and dispensing with the injector 28. The weight of this column resting on the cathode is advantageous in that it serves to bring the electrolyte and liquid metal into close contact.

The arrangement shown in Fig. 3 is similar to those already described, with the exception that the electrolyzing-current is passed in a reverse direction—that is, from the liquid metal—through the electrolyte. In this figure 52 represents a vessel having a partition 53, both of non-conductive material, and a horizontal diaphragm 54. The body 55 of molten lead extends beneath the diaphragm and to a higher level at one side of the partition. Electrolyte 56 fused sodium chlorid floats upon the lead and contains the cathode 59. Upon the other surface of the molten lead is a body of molten-lead chlorid 57, communicating with which is the anode 58. The electrolytic current decomposes the sodium chlorid, liberating the sodium, which may be skimmed off, or if the temperature is sufficiently high removed as a vapor. The chlorin combines with the lead and the lead chlorid flows up into the body of lead chlorid, which is simultaneously electrolyzed, liberating chlorin and returning the lead to receive further addition of chlorin. By depressing the anode 58 into the lead lead chlorid may be continuously produced and drawn off, further additions of metallic lead being then required.

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

1. The process of producing caustic alkali, which consists in providing a liquid-metal cathode having in communication therewith a liquefied alkali-metal compound of a weight sufficient to depress the surface thereof below its normal level, electrolyzing the alkali-metal compound whereby the alkali metal is deposited upon or unites with the depressed surface of the liquid-metal cathode, displacing the liquid metal containing the alkali metal from contact with the liquefied alkali-metal compound by gravity, and removing the alkali metal therein therefrom by the action of a fluid-metal hydroxid.

2. The process of producing caustic alkali, which consists in providing a liquid-metal cathode having in communication therewith a liquefied sodium compound of a weight sufficient to depress the surface thereof below its normal level, electrolyzing the sodium compound whereby the sodium is deposited upon or unites with the depressed surface of the liquid metal, displacing the liquid metal containing the sodium from contact with the liquefied sodium compound by gravity and removing the sodium therein therefrom by the action of fluid sodium hydroxid.

3. The process of producing caustic alkali, which consists in providing a liquid-metal cathode having in communication therewith a liquefied sodium chlorid of a weight sufficient to depress the surface thereof below its normal level, electrolyzing the sodium chlorid whereby sodium is deposited upon or unites with the depressed surface of the liquid-metal cathode, displacing the liquid-metal containing the sodium from contact with the liquefied sodium chlorid by gravity and removing the alkali metal therein therefrom by the action of fluid sodium hydroxid.

4. The process of producing caustic alkali, which consists in providing a liquid-lead cathode having in communication therewith a liquefied alkali-metal compound of sufficient weight to depress the surface thereof below its normal level, electrolyzing the alkali-metal compound whereby the alkali metal is deposited upon or unites with the depressed surface of the liquid-lead cathode, displacing the liquid lead containing the alkali metal from contact with the liquefied alkali-metal compound by gravity and removing the alkali metal therein therefrom by the action of fluid-metal hydroxid.

5. The process of producing caustic alkali, which consists in providing a liquid-metal cathode having in communication therewith a liquefied alkali-metal compound of a weight sufficient to depress the surface thereof below its normal level, electrolyzing the alkali-metal compound whereby the alkali metal is deposited upon or unites with the depressed surface of the liquid-metal cathode, displacing the liquid metal containing the alkali metal from contact with the liquefied alkali-metal compound by gravity and removing the alkali metal therein therefrom by the action of fluid-metal hydroxid.

6. The process of producing caustic alkali, which consists in providing a liquid-metal cathode having in communication therewith a liquefied alkali-metal compound of a weight sufficient to depress the surface thereof below its normal level, electrolyzing the alkali-metal compound whereby the alkali metal is deposited upon or unites with the depressed surface of the liquid-metal cathode, displacing the liquid metal containing the alkali metal from contact with the liquefied alkali-metal compound by gravity and removing the alkali metal therein therefrom by the action of fluid-metal hydroxid.

which consists in providing a liquid-lead cathode having in communication therewith liquefied sodium compound of sufficient weight to depress the surface thereof below its normal level, electrolyzing the sodium compound whereby the sodium is deposited upon or unites with the depressed surface of the liquid-lead cathode, displacing the liquid lead containing the sodium from contact with the liquefied sodium compound by gravity and removing the sodium therein therefrom by the action of fluid-metal hydroxid.

6. The process of producing caustic alkali, which consists in providing a liquid-lead cathode having in communication therewith liquefied sodium chlorid of sufficient weight to depress the surface thereof below its normal level, electrolyzing the sodium chlorid whereby the sodium is deposited upon or unites with the depressed surface of the liquid-lead cathode, displacing the liquid lead containing the sodium from contact with the liquefied sodium chlorid by gravity and removing the sodium therein therefrom by the action of sodium hydroxid.

7. The process of producing caustic alkali, which consists in providing a liquid-metal cathode having in communication therewith a liquefied alkali-metal compound together with an inert granulated diaphragm, the whole of a weight sufficient to depress the surface thereof below its normal level, electrolyzing the alkali-metal compound whereby the alkali metal is deposited upon or unites with the depressed surface of the liquid-metal cathode, displacing the liquid metal containing the alkali metal from contact with the liquefied alkali-metal compound by gravity, and removing the alkali metal therein therefrom by the action of a fluid-metal hydroxid.

8. The process of producing caustic alkali, which consists in providing a liquid-metal cathode having in communication therewith a liquefied sodium compound together with an inert granulated diaphragm, the whole of a weight sufficient to depress the surface thereof below its normal level, electrolyzing the sodium compound whereby the sodium is deposited upon or unites with the depressed surface of the liquid-metal cathode, displacing the liquid metal containing the sodium from contact with the liquefied sodium compound by gravity, and removing the sodium therein therefrom by the action of fluid-metal hydroxid.

9. The process of producing caustic alkali, which consists in providing a liquid-metal cathode having in communication therewith liquefied sodium chlorid together with an inert granulated diaphragm, the whole of a weight sufficient to depress the surface thereof below its normal level, electrolyzing the sodium chlorid whereby the sodium is deposited upon or unites with the depressed surface of the liquid-metal cathode, displacing the liquid metal containing the sodium from contact with

the sodium chlorid by gravity, and removing the sodium therein therefrom by the action of fluid-metal hydroxid.

10. The process of producing caustic alkali, which consists in providing a liquid-metal cathode having in communication therewith a liquefied alkali-metal compound together with a diaphragm of granulated magnetite, the whole of a weight sufficient to depress the surface thereof below its normal level, electrolyzing the alkali-metal compound whereby the alkali metal is deposited upon or unites with the depressed surface of the liquid-metal cathode, displacing the liquid metal containing the alkali metal from contact with the liquefied alkali-metal compound by gravity, and removing the alkali metal therein therefrom by the action of a fluid-metal hydroxid.

11. The process of producing caustic alkali, which consists in providing a liquid-metal cathode having in communication therewith a liquefied sodium compound together with a diaphragm of granulated magnetite, the whole of a weight sufficient to depress the surface thereof below its normal level, electrolyzing the sodium compound whereby the sodium is deposited upon or unites with the depressed surface of the liquid-metal cathode, displacing the liquid metal containing the sodium from contact with the liquefied sodium compound by gravity, and removing the sodium therein therefrom by the action of fluid-metal hydroxid.

12. The process of producing caustic alkali, which consists in providing a liquid-metal cathode having in communication therewith liquefied sodium chlorid together with a diaphragm of granulated magnetite, the whole of a weight sufficient to depress the surface thereof below its normal level, electrolyzing the sodium chlorid whereby the sodium is deposited upon or unites with the depressed surface of the liquid-metal cathode, displacing the liquid metal containing the sodium from contact with the sodium chlorid by gravity, and removing the sodium therein therefrom by the action of fluid-metal hydroxid.

13. The process of electrolyzing metal compounds, which consists in providing a liquid-metal cathode having in communication therewith a diaphragm of granulated inert material together with a liquefied metal compound, electrolyzing the metal compound whereby the metal is deposited upon or unites with the liquid-metal cathode, and discharging the electronegative products liberated within the metal compound therefrom by the combined action of the granulated substance of the diaphragm, and gravity.

14. The process of electrolyzing light-metal compounds, which consists in providing a liquid-metal cathode having in communication therewith a diaphragm of granulated inert material together with a liquefied light-metal compound, electrolyzing the light-metal com-

pound whereby the light metal is deposited upon or unites with the liquid-metal cathode, and discharging the electronegative products liberated within the light-metal compound therefrom by the combined action of the granulated substance of the diaphragm, and gravity.

15. The process of electrolyzing sodium compounds, which consists in providing a liquid-metal cathode having in communication therewith a diaphragm of granulated inert material together with a liquefied sodium compound, electrolyzing the sodium compound

whereby the sodium is deposited upon or unites with the liquid-metal cathode, and discharging the electronegative products liberated within the sodium compound therefrom by the combined action of the granulated substance of the diaphragm, and gravity.

In testimony whereof I affix my signature in presence of two witnesses.

HENRY SPENCER BLACKMORE.

Witnesses:

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ALBERT W. SIOUSSA.