

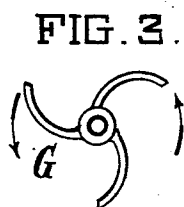
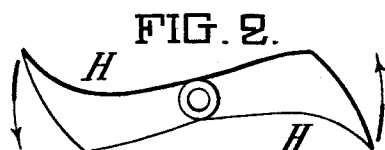
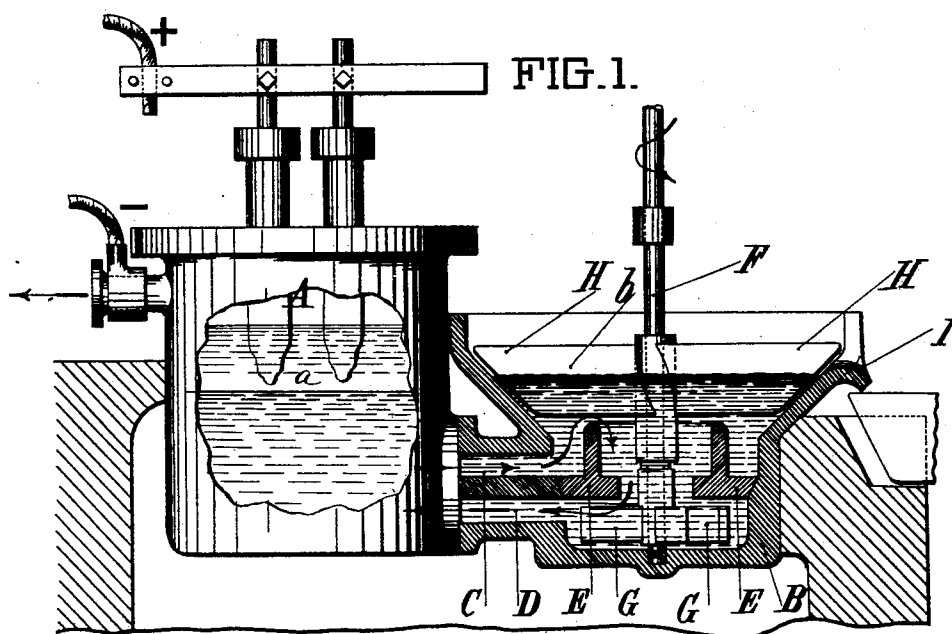
(No Model.)

L. P. HULIN.

PROCESS OF AND APPARATUS FOR MANUFACTURING METALLIC PEROXIDS
AND CAUSTIC ALKALIES.

No. 587,830.

Patented Aug. 10, 1897.



Witnesses:
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UNITED STATES PATENT OFFICE.

LÉON PAUL HULIN, OF MODANE, FRANCE.

PROCESS OF AND APPARATUS FOR MANUFACTURING METALLIC PEROXIDS AND CAUSTIC ALKALIES.

SPECIFICATION forming part of Letters Patent No. 587,830, dated August 10, 1897.

Application filed December 26, 1894. Serial No. 532,909. (No model.) Patented in France May 8, 1894, No. 238,374, and in Belgium May 8, 1894, No. 109,869.

To all whom it may concern:

Be it known that I, LÉON PAUL HULIN, of Modane, Savoy, France, have invented certain new and useful Improvements in Processes of and Apparatus for Manufacturing Metallic Peroxids and Caustic Alkalies, (for which I have received Letters Patent in France, dated May 8, 1894, No. 238,374, and in Belgium, dated May 8, 1894, No. 109,869,) of which the following is a specification.

The invention which forms the subject of the present application for Letters Patent consists in a process and apparatus for the conjoint production of peroxids of certain heavy metals combined with anhydrous protoxids of the alkali and alkali-earth metals. The heavy metals to which my process applies are those of which the higher oxids play the part of an acid, but which cannot be transformed into these acid peroxids by the mere calcination of the metal alone in contact with air. Such are lead, antimony, chromium, manganese, &c.

Succinctly defined and characterized my process consists in alloying the heavy metal to be peroxidized with an alkali metal or alkali-earth metal, heating the alloy to about a dull-red heat and in contact with the oxygen of the air, whereby the alloy becomes oxidized, the product of the oxidation being a combination of peroxid of the heavy metal and of protoxid of the alkali metal.

The acid function of the peroxids of the heavy metals above indicated is so strongly promoted by the oxidation of the alkali metal in the state of alloy that I consider my process is susceptible of replacing that which consists in peroxidizing the heavy metals by calcining one of their lower oxids with an alkali nitrate. For greater clearness and precision in the description of the operations I will hereinafter describe, by way of example, the manufacture of peroxid of lead combined with soda.

I take an alloy of lead and sodium of any origin. Theoretically this alloy should be formed of equal equivalents of lead and sodium; but in practice I prefer that the alloy should be richer in lead than in sodium in order that it may be easily handled and because the operation is better performed. The alloy is fused at a temperature verging on a dull red in an iron vessel expressly arranged for

the access of air. Under these conditions there forms upon the surface of the fused bath a deep-brown scum composed of the anhydrous oxid of the alkali metal united with a variable quantity of lead oxid; but while the alkali metal has remained in a state of protoxid the lead has passed into the state of dioxid—that is to say, to a degree of oxidation superior to that which would be produced by the same temperature out of the presence of the alkali metal which accompanies it in the alloy. Under these circumstances the lead thus becomes peroxidized by the contact of the air at an elevated temperature by favor of the alkali metal with which it is associated. The peroxid and alkaline oxid are combined together, and they form a brown pasty or liquid layer on the surface of the alloy. This layer, which forms my first product, should be removed at regular intervals, so as to expose the alloy to the air and permit the latter to further oxidize it. This skimming may be performed either by hand or by suitable mechanical means, such as that hereinafter described with reference to the apparatus. The composition of the plumbate thus obtained is variable, and it may contain more or less alkali in excess, which depends on the manner in which the operation is conducted. If the products of the oxidation be rapidly removed, a maximum of peroxid of lead is obtained, but if the layer of oxid were allowed to cover the alloy the subjacent alkali metal would be oxidized at the expense of the peroxid of lead which covers it and which would become reduced to the metallic state and return into the alloy, so that I should then obtain a compound richer in alkali but containing much less peroxid of lead than in the previous case. It is in consequence therefore of this retrograde action that I remove the product as rapidly and uninterruptedly as possible. This retrogression is the cause of the product not being an anhydrous plumbate of soda containing well-defined proportions of acid and base. After the operation there remains an excess of metallic lead still containing a little alkali metal, which is utilized in the manufacture of more alloy.

Such, then, are in principle the fundamental characteristics of my process. The

first result is, as before explained, the formation of an alkali compound of a metallic acid, (plumbate, chromate, antimoniate, &c.) These products may either be disposed of for use as such in other manufactures or be treated for the separation of the acid metallic peroxid from the alkali. This separation may be effected by different means, which vary according to the nature of the compound to be decomposed.

In order to decompose plumbate of soda, I digest it in a sufficient quantity of water, whereby the oxid of the alkali becomes hydrated and dissolves with disengagement of heat, giving up the peroxid of lead in the state of a very fine powder resembling a precipitate. On letting rest the peroxid powder deposits and may be separated by decantation or filtration, and it is then washed in pure water, which serves again for the succeeding operation. The peroxid of the heavy metal is then dried (if necessary) and the caustic soda is recovered from its solution by evaporation, as now practiced, or is utilized without further treatment. A more generally-known process consists in substituting lime for the alkali and digesting this base in a solution of the alkali salt of a metallic acid, (chromate, antimoniate, &c.) then separating the solution of caustic alkali which has been freed from the insoluble lime salt of a metallic acid which is formed, and, lastly, liberating the peroxid by saturating the lime by means of a suitable acid, such as hydrochloric, nitric, acetic acids, &c.

In describing the fundamental operations I have supposed them to be intermittent and capable of being performed without any special apparatus.

I will now proceed to describe the combination of my process with the electrolytic production of alloy, thus forming a continuous operation for the production of metallic peroxids and alkali oxids upon the principle herein described. The apparatus which I employ in this case is illustrated by way of example in the accompanying drawings for the purpose of clearly showing how my system is practically applied to an electrolytic or metallic crucible by adapting it to my purpose and also the mechanical arrangements for insuring the continuity of the manufacture.

In the drawings, Figure 1 is a sectional elevation of an electrolytic apparatus for carrying out my invention. Fig. 2 is a plan view of a scraping device forming part thereof; and Fig. 3 is a plan view of a stirrer, also forming part of my apparatus.

A is an electrolytic apparatus for producing an alloy of lead and sodium by the electrolysis of sea-salt (for example) in a state of igneous fusion, which apparatus, considered separately, may be of any principle or system. The fused alloy is maintained at, say, the level *a*. At one side of this crucible the special apparatus B of my invention is ap-

plied, in which is produced and from which is extracted the peroxid of lead united with oxid of sodium. The apparatus B consists of an inverted open conical vessel communicating at its bottom by means of two superposed passages C D with the lower apparatus of the electrolytic part, these channels serving to intimately connect the two parts of the apparatus. The alloy is maintained at a sufficient height to prevent the electrolyte passing through the channel C, so that the alloy alone passes into B, which is almost completely filled, say up to the level *b*, more or less.

E is a diaphragm provided with a large opening at its center, which divides chamber B into two superposed spaces communicating by said opening. A cylindrical partition open at its upper end rises from the diaphragm E.

F is a vertical shaft on which are mounted, first, in the lower chamber a pallet-wheel G, (shown in plan in Fig. 3,) and, second, in the conical portion of the upper part of the chamber curved inclined pallets or scrapers H, (shown in elevation in Fig. 1 and in plan in Fig. 2,) which scrape the conical sides of the chamber. I is an overflow-spout at one side of said chamber.

The action of the apparatus will be readily understood. The electrolytic crucible being in normal operation and charged with alloy, the shaft F is rotated so as to cause the wheel G to carry the bath of molten alloy in the direction of the arrows and bring it in contact with the air, and immediately the layer of oxids *b*—that is, the anhydrous splumbate of soda—forms upon the surface the blades H in revolving immediately project said oxids toward the sides and by their inclined form cause them to rise up the sides and overflow at the spout I into a receptacle. The impoverished alloy returns through channel D into A to be again enriched and returns through G to be oxidized in a continuous manner.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, I declare that what I claim, and desire to secure by Letters Patent, is—

1. The herein-described process of forming the higher peroxids of heavy metals such as lead, antimony, bismuth, chromium and manganese, which are incapable of being separately peroxidized to the maximum by calcination in air, which process consists in alloying said metals with an alkali metal or alkali-earth metal and subjecting the alloy thus constituted to the action of heat and of atmospheric air to form the peroxid desired in combination with the anhydrous alkaline oxid formed conjointly therewith, and decomposing the salt of the metallic acid thus formed in order to separate the peroxid.

2. The herein-described process of forming the higher peroxids of heavy metals such as lead, antimony, bismuth, chromium and manganese, which are incapable of being sepa-

ately peroxidized to the maximum by calcination in air, which process consists in alloying said metals with an alkali metal or alkali-earth metal and subjecting the said alloy thus constituted to the action of heat and of atmospheric air to form the peroxid desired in combination with the anhydrous alkaline oxid formed conjointly therewith and continuously withdrawing the said peroxid and alkaline oxid from the presence of the alloy under treatment in order to prevent the sodium remaining in the alloy from reducing the peroxid formed which would occur if the peroxid were allowed to remain in company with the alloy.

3. The herein-described process of producing the higher peroxids of heavy metals such as lead, antimony, bismuth, chromium and manganese, which consists in alloying the heavy metal to be peroxidized with an alkali metal or alkali-earth metal, heating the alloy to about a dull-red heat in contact with oxygen, whereby the alloy becomes oxidized, producing a combination of peroxid of the heavy metal and a protoxid of the alkali metal, substantially as described.

4. The combination of an oxidizing vessel provided with a stirrer, circulating-channels

and a discharging scraper or scrapers for the oxidized product, with an apparatus for the continuous production of the alloy required for carrying out the process described.

5. The herein-described process of producing the higher peroxids of heavy metals, and an alkaline protoxid which consists in subjecting an alloy composed of the heavy metal to be peroxidized and an alkali metal or alkali-earth metal to the action of an electric current of such volume as to produce a fused bath of said alloy, exposing the said alloy while in such molten condition to the action of oxygen, thereby producing a peroxid of the heavy metal and a protoxid of the alkali metal or alkali-earth metal, producing a circulation of the fused bath and removing the peroxid and protoxid formed from the presence of the molten alloy.

The foregoing specification of my process of and apparatus for the conjoint manufacture of metallic peroxids and caustic alkalies signed by me this 3d day of December, 1894.

LÉON PAUL HULIN.

Witnesses:

CLYDE SHROPSHIRE,
ALBERT MOREAU.