

# UNITED STATES PATENT OFFICE.

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ELECTROLYTIC PROCESS OF MAKING BASES OF THE ALKALI-EARTH METALS.

No. 835,661.

Specification of Letters Patent.

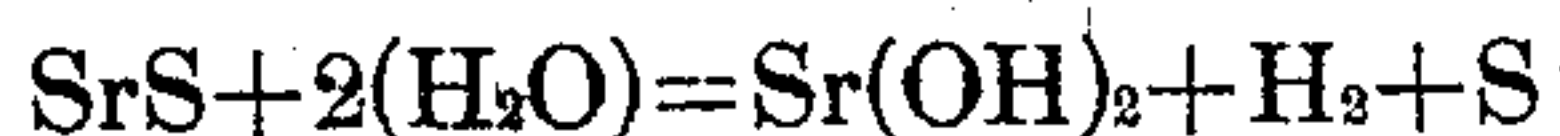
Patented Nov. 13, 1906.

Application filed February 14, 1901. Serial No. 47,253.

*To all whom it may concern:*

Be it known that we, ANDRÉ BROCHET and GEORGES RANSON, citizens of the Republic of France, residing at Paris, France, have invented certain new and useful Improvements in Electrolytic Processes for Making Bases of the Alkaline Earths; and we do declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

Our process consists, essentially, in electrolyzing a mixture of the sulfids of the alkaline earths with chlorids. Under these circumstances hydrate of the alkaline earth is formed at the cathode and a deposition of sulfur takes place at the anode without any chlorine being given off and without the drawbacks resulting therefrom. The addition of the chlorid of an alkaline earth to the sulfid has for its object to facilitate the reaction. A small quantity of chlorid serves for an indefinite period, and the final electrolytic reaction may be represented in the following way:



The whole or a part of the chlorid of the alkaline earth may be replaced by the chlorid of an alkali; but if a diaphragm be used in such a case, the said chlorid of an alkali passing into the cathode-compartment, it is preferable to introduce it therein directly. Likewise in order to obtain directly the base of the alkaline earth in the pure state the sulfid may be placed in the anode-compartment only and the chlorid of an alkali metal employed in solution in the cathode-compartment. The cathode may be of any kind.

When an insoluble anode is employed—carbon, for instance—sulfur is deposited more or less mixed with sulfids, sulfites, and sulfates of the alkaline earths.

When a soluble anode is used—for instance, iron or copper—an insoluble sulfid is obtained directly, so that the metallic salt when precipitated has no action upon the metallic base, which becomes diffused in the anode-compartment and which can be recovered subsequently, because it is not destroyed in that compartment. Likewise when insoluble anodes are used the diaphragm serves no other purpose than to enable the bases to be obtained directly in a pure state.

When a diaphragm is employed, the operations take place in the following manner: The cathode liquid, which was formed originally of a solution of a chlorid of an alkali or of a chlorid of an alkaline earth, flows in a continuous manner into the apparatus, becomes charged with the base of the alkaline earth, and on passing out is led into crystallizing apparatus in which the base of the alkaline earth becomes deposited by cooling. The latter is separated by centrifugal action in a suitable separator from the mother-liquor, which is returned to the apparatus, &c. The anode liquid, consisting of a mixture of the sulfid of an alkaline earth and of a chlorid of an alkali or of an alkaline earth, may be when needed conducted from the apparatus and filtered, reheated, and subjected to systematic lixiviation in the presence of the sulfid of an alkaline earth, whereby it may be kept saturated. This operation may be performed in any preferred way.

In order to prevent the carbonic acid of the atmosphere from having any action upon the alkali in the cathode-compartments, we cover the surface of the liquid with a thin layer of paraffin, petroleum, vaseline-oil, or other substance, which is not acted upon by alkalies.

As above stated, the addition of an alkaline chlorid to the sulfid or as catholyte has for its object to facilitate the reaction. The use of said substance diminishes the resistance at the beginning of the operation, said resistance being relatively high at this moment, owing to the small quantity of the base which is present in the solution. Further, the use of said substance as catholyte enables of obtaining the base of the alkaline earth in a pure state at the cathode, or, in other words, free from sulfid, and the quantity of the base obtained is improved, for the reason that in case there is made use of a diaphragm, for instance, it is the "chlorid radical" (Cl) which is passing to the anode, the base being formed at the cathode. The use of the alkaline chlorid has further the purpose, when a soluble anode is made use of, of dissolving said anode in such a manner as to form a chlorid of the metal of the anode, which immediately decomposes with the sulfite of the alkaline earth into sulfid of the metal of the anode and sulfur, which are separated in the anode-compartment.

We are aware that sulfids of the alkaline have already been subjected to electrolysis,



as antimony double salt, for recovery of the antimony in metallic form; but in said process it was impossible to obtain the hydrate of the alkaline earth at the cathode, as is clearly shown by the reaction taking place in the baths on the cathode. We therefore do not claim, broadly, the process of electrolyzing the sulfids of the alkaline; but,

Having thus described our invention, what we claim, and desire to secure by Letters Patent, is—

1. The herein-described process for the production of hydrate of the alkaline earths which consists in electrolyzing an anode liquid, composed of a solution of sulfid of an alkaline earth and a cathode liquid composed of a solution of chlorid of an alkaline earth, interposing a suitable diaphragm between said solutions, then charging the solution of the chlorid of the alkaline earth with the base of the alkaline earth, then effecting the crystallization of said charged solution and finally causing the base of the alkaline earth to be deposited by cooling substantially as described and for the purpose set forth.

2. The herein-described process for the production of hydrate of the alkaline earths which consists in electrolyzing an anode liquid, composed of a solution of sulfid of an alkaline earth, and a cathode liquid composed of a solution of chlorid of an alkaline earth, interposing a suitable diaphragm between said solutions causing the solution of the chlorid of the alkaline earth to circulate in a continuous manner during the electrolysis, thereby charging the solution of the chlorid of the alkaline earth with the base of the alkaline earth, then effecting the crystallization of

said charged solution, then causing the base of the alkaline earth to be deposited by cooling substantially as described and for the purpose set forth.

3. The herein-described process for the production of hydrate of the alkaline earths which consists in electrolyzing an anode liquid, composed of a solution of sulfid of an alkaline earth, and a cathode liquid composed of a solution of chlorid of an alkaline earth interposing a suitable diaphragm between said solutions causing the solution of the chlorid of the alkaline earth to circulate in a continuous manner during the electrolysis, thereby charging the solution of the chlorid of the alkaline earth with the base of the alkaline earth, then effecting the crystallization of said charged solution, then causing the base of the alkaline earth to be deposited by cooling, then separating the base from the mother liquid, then reexposing the latter to the electrolyzing-current, causing simultaneously with these operations the solution of the sulfid of alkaline earth to circulate in a continuous manner during the electrolysis and finally filtering said solution, reheating and saturating the same with the sulfid of the alkaline earth before being reexposed to the electric current.

In testimony whereof we have hereunto set our hands in presence of two subscribing witnesses.

ANDRÉ BROCHET.  
GEORGES RANSON.

Witnesses:

LOUIS BAUDART,  
ANTOINE AUGIER.