

UNITED STATES PATENT OFFICE.

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PROCESS OF MANUFACTURING BARIUM CHLORID.

1,167,061.

Specification of Letters Patent.

Patented Jan. 4, 1916.

No Drawing.

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To all whom it may concern:

Be it known that I, EINAR VANG GRANÖ, a citizen of the United States, residing in Leonia, county of Bergen, and State of New Jersey, have invented new and useful Improvements in Processes of Manufacturing Barium Chlorid, of which the following is a specification.

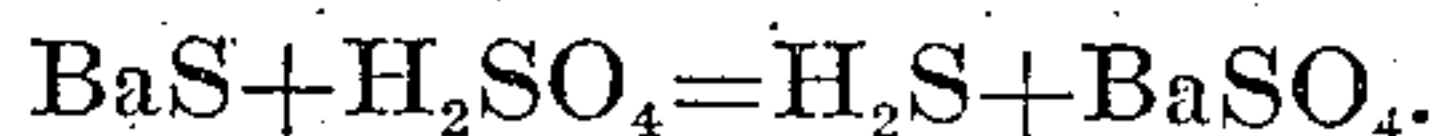
This invention relates to the manufacture of barium chlorid from barium sulfid obtained by the reduction of barytes (native barium sulfate) or from any other source and has for its objects the production of substantially quantitative yields of the said barium chlorid by an extremely simple and yet effective method at a minimum cost.

Heretofore it has been proposed to prepare barium chlorid by double decomposition of barium sulfid and a soluble chlorid, such as zinc chlorid, but among the objections to such process was the difficulty and cost of obtaining the necessary raw products in sufficient quantities in the outlying localities where it is necessary to set up plants for its production if the commercial manufacture is to be successful.

I discovered that not only can a substantially quantitative yield of barium chlorid be obtained by the reaction of the chlorin gas (either obtained by electrolysis or otherwise) upon a strong solution of barium sulfid obtained by the reduction in the well known manner of barytes with carbon and subsequent leaching of the furnaced product with water, but that the employment of this method enables this process to be carried out in conjunction with other profitable processes wherein chlorin gas is obtained as a by-product. Moreover, in addition to obtaining a quantitative yield of barium chlorid, a substantially quantitative yield of sulfur in a finely precipitated condition can be obtained.

In carrying out my invention I preferably proceed as follows:—A concentrated solution of barium chlorid is employed, preferably of specific gravity 20° Bé., the same being maintained at a temperature of about 85° C. The foregoing density and temperature are desirable to prevent crystallization of barium hydroxid $\text{Ba}(\text{OH})_2$, such solution containing approximately 178 grams of BaS per liter. Electrolytic chlorin gas is conducted into the solution, while the same is maintained at the aforesaid temperature of approximately 85° C., and at a point a

sufficient distance from the bottom of the body of liquid to permit the precipitated sulfur to settle to the bottom below the depth to which the agitating effect of the gas is liable to exert its influence or effect reaction. The object of this arrangement is to prevent the sulfur liberated by the chlorin gas from coming in contact with an excess of chlorin whereby there would be a possibility of the formation of small quantities of sulfuric acid. Such acid would obviously instantaneously decompose a corresponding amount of BaS according to the following reaction:



To prevent the sulfur already formed from being acted upon by the chlorin gas in the aforesaid manner, a perforated false bottom is inserted in the precipitating vessel at a suitable depth below the lower end of the pipe carrying the chlorin. The openings in this false bottom are $\frac{1}{4}$ inch in diameter there being 5 or 6 to the square inch, this being sufficient to permit the sulfur to sink through to the bottom of the precipitating vessel. Preferably in a cylindrical tank 9 feet high by 3 feet in diameter containing liquid to a height of approximately 8 feet, a pipe 1 inch in diameter projects into the middle of the tank to a point 1½ feet above the false bottom of said tank, the said false bottom being in turn placed 1 foot above the real bottom. By such arrangement the agitating action of the gas will cause all sulfur as formed to pass through the perforated bottom after which it will not be reacted upon by the free chlorin, since the same will penetrate but little if at all below said bottom, the pressure under which the chlorin is introduced being adjusted to produce the desired agitation.

To insure that all the BaS will be reached, the liquid may be agitated by a pump, which draws it from a point at the bottom of the tank and after passing it either through a filter to collect the sulfur or through a settling tank where the sulfur is deposited, returns it to the precipitating tank. This movement of the liquid will help to carry the precipitated sulfur through the said false bottom. An exhaustive investigation of the aforesaid process showed that in order to determine to what extent this acid reaction (the oxidation of sulfur by chlorin to sul-

furic acid) will take place when the chlorin by being conducted into the bottom of the vessel is given every opportunity to react upon the nascent sulfur, shows that there
5 will be as high as 12% of the total sulfur oxidized to sulfuric acid, whereas by my invention less than 2% of sulfur was so converted into sulfuric acid. During the first stages of the reaction it will be observed
10 that the sulfur liberated by the chlorin appears to be partly dissolved by the remaining BaS, the color of the solution being a deep reddish yellow or orange indicating the presence of polysulfids, these being
15 known to possess a strong color in concentrated solutions. As the reaction progresses further these polysulfids are in turn decomposed and toward the end of the process it will be found that the major part of the
20 barium ion has been combined with the chlorin while the sulfur is precipitated in ever increasing quantity so that when the process is finally completed the color of the liquid loses its yellow tint almost instantaneously and becomes clear, whereas the

precipitated sulfur will then appear of a pale yellow or almost white color.

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

1. The process which consists in subjecting a solution of barium sulfid to the action of chlorin gas conducted into said solution from an external source, then permitting the same to react while constantly removing
35 from the zone of influence of said chlorin gas, the sulfur resulting from said reaction, and then separately recovering the barium chlorid and sulfur from said mixture.

2. In the process of making barium
40 chlorid and sulfur the steps which consist in conducting chlorin gas into a concentrated solution of barium sulfid while maintaining the solution at a temperature sufficiently high to prevent crystallization of
45 the barium hydroxid from said solution.

Signed at New York, county and State of New York, this first day of May, 1915.

EINAR VANG GRANÖ.