

UNITED STATES PATENT OFFICE.

HUBERT GROUVEN, OF LEIPSIC, SAXONY, GERMANY.

MANUFACTURE OF STRONTIUM CARBONATE.

SPECIFICATION forming part of Letters Patent No. 280,172, dated June 26, 1883.

Application filed May 1, 1883. (No specimens.)

To all whom it may concern:

Be it known that I, HUBERT GROUVEN, of Leipsic, Kingdom of Saxony, German Empire, have invented an Improvement in the Manufacture of Carbonate of Strontium, of which the following is a specification.

The perfect reduction of coelestin or sulphate of strontium into sulphide of strontium by means of carbon requires a degree of white heat which will destroy the crucible, so that it can only be used once. Moreover, the decomposition of sulphide of strontium by carbonic acid is difficult and only partial, and hence the sulphide of strontium, or the cheap sulphate in the form of coelestin, has never been used successfully in the manufacture of strontia on a commercial scale. I remove the difficulties by introducing sulphide of potassium into the process. Sulphide of potassium, being a body which, at a glowing heat, considerably surpasses the reducing-power of carbon, will, in connection or combination with carbon, completely reduce the coelestin at a comparatively low temperature.

I have ascertained that, in connection with sulphide of potassium, the sulphide of strontium will more easily dissolve in boiling water than sulphide of strontium alone. I have, furthermore, ascertained that the decomposition of a hot solution of sulphide of strontium and sulphide of potassium by carbonic acid takes place more rapidly and more completely than when treating each part with carbonic acid separately. I introduce the sulphide of potassium into the process by mixing powdered coelestin with finely-powdered crystallized double salt of sulphate of potassium and magnesium. These are heated to incandescence in connection with carbon, and the double salt will be reduced first, and at a comparatively low temperature, into oxide of magnesium and sulphide of potassium. The latter, which is easily fusible, will act on the adjacent molecules of coelestin. I have found that the mixture for said process is preferably made in the following proportions: one hundred and ninety to two hundred kilograms of powdered coelestin, equal to two atoms of sulphate of strontium; two hundred and two to two hundred and five kilograms of the crystallized double salt of potassium and magnesium, equal to one atom of

sulphate of potassium and magnesium; one hundred and fifty kilograms of powdered coal, (gas-coal;) ten to fifteen kilograms of sulphate of potassium residuum of the preceding process. These materials must be finely powdered and very intimately mixed and ground together, and are furnaceed or brought to incandescence, the air being perfectly excluded. I preferably execute this furnaceing process in cast-iron cylindrical crucibles of about one hundred and ten millimeters internal diameter and eight hundred millimeters height, which crucibles are suspended in rows in the top of a crucible furnace heated by generator-gases and superheated air. After each furnaceing, lasting about two hours and a half, one series of incandescent crucibles is removed from the top of the furnace and replaced by a new series freshly charged.

A crucible of the dimensions mentioned holds eight liters, and contains the above standard mixture, with five kilograms of coelestin. In the upper part of the sides of each crucible, but below the top of the furnace, several holes are provided, each ten millimeters in diameter, through which the carbonic-oxide gas and sulphureted-hydrogen gas, developing in abundance during the furnaceing process, will escape, and will burn in the oven, thereby helping to heat it. Outside the oven the crucible is closed, during the furnaceing, with a loose cover, which may be easily made gas-tight with clay in the well-known manner. This very important desulphuration of the contents of the crucibles, which is indicated by the above-mentioned abundant development of sulphureted-hydrogen gas, depends upon the six to seven kilograms of hydrogen contained in the powdered coal, steadily and slowly set free from the same during the furnaceing process. The temperature in the oven must not be above the melting-point of copper. The crucibles will stand such a heat well, especially if made of the best Scotch iron, and will be but slowly destroyed. The inside of them is not corroded at all by the above-named mixture, which, during the furnaceing, is not melted, but simply forms into a lump, which, on turning over the crucible, will at once fall out and show a soft flesh-color mass. This mass, which, for convenience, I will call "sulphide mass," if fur-

naced properly, will weigh about two hundred and fifty kilograms. It should dissolve entirely in diluted hydrochloric acid, and should contain neither sulphuric acid nor any white particles of undecomposed coelestin. This sulphide mass is composed of magnesia, hydrated oxide of strontium, sulphide of strontium, and sulphide of potassium, and is directly poured from the cooled crucibles into the extraction-vessels, whereby exposure to air is avoided as much as possible. These extraction-vessels are closed, and preferably round, and each is provided with an agitator and a steam-coil for boiling the mass. The lixiviation, in a boiling state, is continued by decantation and repeated pouring on of fresh water until the filtered fluid will only show traces of oxide of strontium. I prefer to combine seven of such vessels, so as to obtain continuous lixiviation and concentrated filtrates. These filtrates are clear, nearly colorless, and, if cooled down, more than one-half of the strontium will be separated in large crystals, as hydrate of strontia. This oxide, however, will prove to be polluted with a small quantity of sulphide of strontium, for which reason I prefer not to separate the oxide, but to convert it, in connection with the mother-lye, into carbonate of strontium. This conversion of the solution of strontium and sulphide of potassium into carbonate of strontium and carbonate of potassium is obtained by introducing carbonic acid at boiling-point, so that the result will be, on the one hand, a heavy sediment of carbonate of strontia, and, on the other hand, a ten per cent. solution of carbonate of potash. The development of sulphureted-hydrogen gas, which is enormous at the start, diminishes gradually after a few hours' continuance of this operation. This introduction of carbonic acid may be stopped as soon as a strip of paper moistened with a solution of acetate of lead will not indicate any trace of hydrosulphureted hydrogen in the escaping vapors. The carbonic acid to be used must be free from any oxygen gas or smoke, and the perfectly-pure carbonic acid obtained by acting with superheated steam upon limestone is to be preferred. The precipitated carbonate of strontium is to be separated from the potash solution by a filter-press, and may easily be lixiviated, so as to leave it as a white coke. It

contains ninety-nine per cent. of carbonate of strontium and only very little sulphide of iron. The potash solution, after evaporation, roasting, and redissolving in a minimum of cold water, whereby small quantities of oxide of iron and sulphate of potassium are left, will give a potash of ninety-eight per cent. if the double sulphate of potassium and magnesium employed has been nearly free of chlorides. The small portion of sulphate of potassium thus left is added to the next mixture for the crucible, and, re-entering into the process, is not lost. According to the process described, I gain from each one hundred kilograms of coelestin about sixty-six kilograms of carbonate of strontium and twenty-eight kilograms of carbonate of potassium. The latter will cover about two-thirds of the entire cost of manufacturing, and therefore the manufacture of the carbonate of strontium is made uncommonly cheap.

I claim as my invention—

The method herein specified of manufacturing carbonate of strontium, consisting, first, in mixing powdered coelestin with a double sulphate of potassium and magnesium and powdered carbon or coal, in the proportions mentioned, or nearly in those proportions; second, furnacing this mixture, under exclusion of air, for its conversion into sulphide of strontium, hydrated oxide of strontium, sulphide of potassium, and magnesium in cylinders or crucibles within a furnace; third, the lixiviation of the furnaced mass with water, under exclusion of air, for gaining a solution of hydrated oxide of strontium, sulphide of strontium, and simple sulphide of potassium; fourth, the evaporation of this solution, at the same time introducing carbonic-acid gas till the development of sulphureted-hydrogen gas stops, and separation of the precipitated strontium carbonate from the potassium carbonate left in the solution.

In testimony whereof I have hereunto set my hand, this 27th day of March, 1883, in the presence of two subscribing witnesses.

HUBERT GROUVEN.

Witnesses:

WILHELM WRESCHÜTTER,
GEORG RICHTER.