UNITED STATES PATENT OFFICE.

PIERRE PIPEREAUT AND ANTONY VILA, OF PARIS, FRANCE.

PROCESS OF PRODUCING PURE ZINC SULFID AND THIOSULFATES.

1,013,511. Specification of Letters Patent. Patented Jan. 2, 1912.

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To all whom it may concern:

Be it known that we, PIERRE PIPEREAUT and ANTONY VILA, chemical engineers, citizens of the Republic of France, residing at 13 Avenue des Gobelins, Paris, in the Department of Seine, in the Republic of France, have invented certain new and useful Improvements in Processes of Producing Pure Zinc Sulfid and Thiosulfates, for which we have obtained a patent in Belgium, No. 202,686, dated September 19, 1907, and applied for a patent in Germany, dated November 29, 1907; and we do hereby 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.

This invention relates to an improved process for preparing zinc sulfid and alkali thiosulfates.

It is old to produce zinc sulfid by causing alkaline sulfids to lixiviate with alkaline solution of zinc. The zinc sulfid obtained by this method is very bulky, and is in a sort of collodial form; it can be filtered only with great difficulty, and cannot be washed easily.

We have found that in the case of zinc, it is sufficient to take ores of zinc, blende, calamin, smithsonite, Broken Hill ore, Greensbit ore, etc., and roast them in order to obtain an oxid or roasted product and to subject them to the action of a caustic alkaline lye such as soda. The decanted clear solution is then boiled, and then pulverized sulfur is added to it in the required quantity and sufficient to convert all metals dissolved, except that which is desired to recover, into insoluble sulfids, which are first precipitated as impurities. After the separation of these impurities, to the solution is then added, in small amounts, sufficient sulfur to convert the metal remaining in solution into sulfid. Alkaline sulfid in nascent state is thereby produced.

This process differs entirely from the action of alkaline sulfids, previously manufactured, on alkaline solutions of metals.

In the process according to this invention, the precipitation is not an immediate one, it is the result of a series of progressive transformations terminating finally in the production of the sulfid desired, moreover, it is completed only after long boiling. On the contrary, when the same solutions are precipitated by means of an alkaline sulfid prepared in advance, it is well known that in such conditions the precipitation is immediate and complete. It has been found that zinc sulfid can be obtained in an easily filterable granular state, if one does not heat the alkaline solutions of zinc with already formed, alkaline sulfids, but if one heats these alkaline solutions of zinc, with the sulfur under the conditions described the alkaline sulfid in a nascent state, reacts with the zincates.

This process is applicable to carbonates and compounds of other metals of the zinc group. The compound of metal and alkali reacts then on the nascent sulfid, and the reaction once having been started, continues gradually, as in the case of zinc.

The precipitates obtained by this process are in the form of microscopic grains of great density, the washing and drying operations become very easy, so that it is possible to obtain pure products of unctuousness equal to that of talc, in all cases in which the ordinary processes give merely gelatinous collodial precipitates which it is impossible to wash completely.

Alkaline liquids used for the transformation of oxids of ores into metallic sulfids, can be utilized a great number of times, until the contents of alkaline thiosulfate which is formed as a by-product owing to the long contact with the air becomes so great that it is advisable to effect its crystallization.

If we are examining the example given for zinc sulfid, we find the well known equations:—

$$ZnO+2NaOH=ZnO_2Na_2+H_2O.$$

It is well known that if sulfur is added to a pure boiling alkaline liquor, there are hydrated sulfids formed after the quantities taking part in the reaction: $Na_2S,9H_2O$ (Kircher—*Annal der Ph.:* t. xxxl, p. 339). $Na_2S,5H_2O$ and $Na_2S_3,5H_2O$ (Bottger—*Ann. Ch. Phys. Liebig*—223, 535—1884). $Na_2S_4.6H_2O$ (Schone, *Ann. Ph. Ch. Pogg.* 131, 386—1867). Na_2S_5 and Na_2S_4 (Bloxa. *J. Chem. Sec.* 77, 753—1900). There is also sodium thiosulfate formed $S_2O_2Na_2,5H_2O$. If these hydrated sulfids are added by themselves to a solution of alkaline zincate, there is immediately formed a precipitate of zinc sulfid.

$$ZnO_2Na_2+Na_2S+aq.=ZnS+Na_2O+aq.$$

In the operation described, the sulfur is introduced into the boiling alkaline solu-

tion of alkaline zincate and the zinc sulfid is not immediately precipitated in these circumstances. On the contrary the clear white solution of alkaline zincate darkens immediately to an intense yellow, because of the digesting of a great part of the sulfur but without any formation of a precipitate. It is only after a certain time, which differs under different conditions, that the precipitate of zinc sulfid is formed; this formation of precipitate increases, and the boiling liquid looses slowly its yellow color and is quite colorless when the reaction is finished.

The following equation is given by way of example:

$$S_2+4NaOH=S_2O_4Na_4H_4.$$

This compound, in contact with ZnO_2Na_2 will soon dissociate and give:

$$2S_2O_4Na_4H_4+ZnO_2Na_2= \underset{\text{(nascent)}}{ZnS}+Na_2S+S_2O_3Na_2+6NaOH+H_2O.$$

We use for a quantity of 100 kgs. of molten ore, containing about 30 kgs. of metallic zinc, 80 kgs. of caustic soda diluted in 60 liters of water; the whole is heated in an apparatus of iron plate, or other iron apparatus. We heat to ebullition for 6 hours at 130–140° C.; after cooling we add water to form 100 liters of solution. After 12 hours, 90 liters of clear liquid can be decanted. To this liquor, while boiling we add a small quantity of pulverized sulfur after 3 hours boiling the colored sulfids are precipitated, they are separated; and to the decanted and purified liquor, we add 10 kgs. of pulverized sulfur, and we boil throughout 4 hours to finish the reaction. The zinc sulfid obtained by this method is washed and dried and produces a fine white powder. It is advisable to replace a small fraction of the alkaline lye after each operation.

The operation is carried out in the following way: A solution of zinc oxid in caustic alkali, for instance, NaOH, is made at first; this solution is kept boiling and the quantity of sulfur necessary to form zinc sulfid is added while boiling. At first, the sulfur dissolves without giving any precipitate; after a certain time of heating there is found a granular zinc sulfid precipitate, which settles very well to the bottom and can easily be filtered and washed. Instead of zinc oxid dissolved in alkali one can use also a solution of zinc carbonate in caustic alkali solutions.

Instead of zinc oxid or carbonate, cadmium oxid, carbonate or acetate may be employed in order to obtain in the same manner cadmium sulfid. Alkaline liquid used for the transformation of oxids or ores into unctuous sulfids, can be utilized a great number of times, until the contents of alkaline thiosulfate which is formed as a by-product, owing to the long contact with the air, become so great that it is advisable to effect its crystallizations.

We claim:

1. The process for treating zinc sulfid ore to recover zinc sulfid in a granular form, which consists in lixiviating the ore with caustic alkali solution thereby forming alkali zincate, heating to boiling, adding sufficient free sulfur to precipitate the metals other than zinc, in the form of sulfids, and separating the same from the solution prior to the precipitation of the zinc sulfid and then adding, in small amounts, sufficient free sulfur to precipitate the zinc present, while keeping the liquid hot.

2. The process for treating zinc sulfid ore to recover zinc sulfid in a granular form, which consists in lixiviating the ore with caustic alkali solution thereby forming alkali zincate, heating to boiling, adding sufficient free sulfur to precipitate the metals other than zinc, in the form of sulfids, separating the same from the solution prior to the precipitation of the zinc sulfid and then adding, in small amounts, sufficient free sulfur to precipitate the zinc present, while keeping the liquid hot, and filtering to remove the zinc sulfid.

In testimony whereof we affix our signatures.

PIERRE PIPEREAUT.
ANTONY VILA.

In the presence of—
THEODORE REDIG,
HERMANN LUTHER.