UNITED STATES PATENT OFFICE.

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PROCESS OF TREATING ZINC ORES.

No. 799,743. Specification of Letters Patent. Patented Sept. 19, 1905.

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To all whom it may concern:

Be it known that I, PHILIP A. MACKAY, a citizen of the United States, residing at Wonona, in the county of Marshall and State of Illinois, have invented a certain new and useful Improvement in Processes of Treating Zinc Ores, (Case No. 1,) of which the following is a full, clear, concise, and exact description, reference being had to the accompanying drawings, forming a part of this specification.

My invention relates to a process for refining or treating ores of zinc previous to obtaining zinc in merchantable form, either as spelter or zinc oxid.

My process provides for a preliminary treatment whereby the resulting zinc products will be obtained in a purer state than has heretofore been commercially practicable.

Zinc oxid is reduced by carbon (C) only after a temperature of about 1,300° centigrade is reached, the reaction being

$$ZnO+C=Zn+CO;$$

but zinc volatilizes at a temperature of less than 1,000° centigrade. Therefore the extraction of zinc is possible only by distillation and condensation. This condensation must be effected at a temperature lower than 800° centigrade in order to prevent the escape and loss of zinc-vapor with the gases formed in reduction. These gases, carbon monoxid (CO) and carbon dioxid, (CO_2,) are always associated with zinc-vapor, and they, as well as air and steam present, partially oxidize zinc unless cooled below the above temperature of 800° centigrade. In order to prevent this reduction so far as possible, the ores to be treated must previously be freed from carbonic acid and water by calcination or roasting. In treating the ores in which zinc is present as a sulfid (ZnS) there is a further reason why thorough calcination must first be resorted to. It is the fact that the sulfid of zinc is not attacked by carbon or carbon monoxid. It is therefore necessary to thoroughly roast the ore and reduce the sulfid (ZnS) to the oxid (ZnO) in order that it may later be acted upon by the carbon. There have been a number of processes used to reduce the zinc oxid after this preliminary roasting—such as the old English process, the Silesian, and the Belgian—in all of which the principle has been the same. Taking as an example the Belgian process, it has been the practice to charge clay retorts with a mixture of the roasted and ground oxid and other minerals present and hard-coal screenings in about equal proportions. As is well understood by those skilled in the art, the ores of zinc—such as zincite, calamin, and blende—contain many other substances besides pure compounds of zinc. Thus in addition to zinc sulfid, (ZnS,) blende contains sulfids of iron, (FeS,) lead, (PbS,) antimony, (Sb_2S_3,) and cadmium, (CdS.) These impurities of course are more or less reduced during the roasting process and are then charged into the retorts with the zinc oxid. These retorts are then gradually heated. Each retort is provided with a clay condenser fitted to the end of the retort and projecting through the front wall of the furnace. Each condenser has a basin-like depression for catching the distilled zinc, and at the outer end each condenser is further provided with an iron hood, through a hole in which the gases may escape. As the retort is heated one of the first reactions is that between the cadmium oxid and carbon, $CdO+C=2\,Cd+CO$. The cadmium formed vaporizes at a low temperature and passes off through the retort into the iron hood, where it is partially oxidized by the air and steam present and drops into the hood as oxid and metallic cadmium. As the temperature of the retort increases the zinc begins to distil over. When the complete distillation of the cadmium has taken place (indicated by the cessation of the issue of brown fumes from the orifice of the hood) and when the distillation of the zinc has begun, (indicated by an intense white flame,) then the condenser-hood is removed and the cadmic contents cleaned out; but it has heretofore been impossible to thus obtain cadmium free from impurities, and also a considerable amount of cadmium is found in the zinc collected in the condenser. It is desirable in practice to secure metallic zinc free from cadmium. This is particularly important when the zinc is to be later oxidized to form zinc white for painting purposes, because any cadmium present will form an oxid, which, being of a dark-brown color, lessens the value of the white pigment.

I shall now describe my new process whereby I completely separate cadmium from zinc and secure the latter in its pure state.

In accordance with my invention I charge the bed of a calcining or roasting furnace with zinc ore—such as black-jack—which we may suppose to contain such impurities as sulfids of iron, (FeS,) antimony, (Sb_2S_3,) cadmium, (CdS,) and lead, (PbS.) I then proceed to roast the ore to a dead roast, by which

means I find that the zinc sulfid (ZnS) is completely oxidized.

$$ZnS + 3O = ZnO + SO_2,$$

the sulfur being burned in an excess of oxygen. The iron present is oxidized and will give no further trouble, as it is neither soluble in water nor affected by the degree of heat used in the zinc reduction. The sulfid of antimony is oxidized:

$$Sb_2S_3 + 9O = Sb_2O_3 + 3SO_2,$$

which sulfur is also burned in the excess of oxygen. The sulfids of lead and cadmium are both oxidized by the excess of oxygen or acted upon by the sulfurous-acid fumes to form sulfates.

$$PbS + 4O = PbSO_4$$

and

$$CdS + 4O = CdSO_4.$$

Of these oxids and sulfates formed all are practically insoluble in water with the exception of cadmium sulfate, which is readily soluble. The roasted ore is then treated with water, which dissolves out the cadmium sulfate. The remaining oxids and lead sulfate are then dried and ground and finally distilled in the retort of a Belgian furnace, as above described, except that there is now no cadmium present to be dealt with.

My invention may be particularly advantageously employed when sulfid ores are used as sources of zinc-oxid production. In producing oxid it is the practice after removing as much sulfur as possible by roasting to burn the zinc and to collect the white oxid by passing the fumes through passages intercepted by sheets of cloth.

As was above pointed out, part of the sulfur in the ore remains after roasting in the form of sulfate of cadmium. If lime is present in the ore, sulfur will also remain in the form of $CaSO_4$. With these two sulfates remaining it will be apparent that when the zinc is burned off the sulfur compounds of cadmium and lime are broken up at the intense heat prevailing, and the sulfur-gases passing off with the zinc-vapor combine to form zinc sulfate in the finished zinc oxid, which, being soluble in water, causes paint, in which zinc oxid is used as the pigment, to run on exposure to the weather. Another disadvantage in the above process lies in the fact that in the burning of the zinc the cadmium, which remained as sulfate, will also be volatilized and converted partly into a dark-brown oxid and partly into a bright yellow sulfid, both of which cadmium compounds materially detract from the commercial value of the zinc oxid in which they are contained. Now as the sulfate of cadmium is readily soluble in water it will be seen that by the employment of my new process in which the roasted ore is washed in water this deleterious sulfate is entirely extracted from the zinc compounds. The amount of lime present is usually very small, and as the sulfate of calcium is also slightly soluble in water the calcium sulfate is almost, if not entirely, removed with the cadmium sulfate from the remaining zinc compound. This leaves the residue free from sulfur and free from cadmium, the advantages of which have been pointed out.

While I have particularly described the process of my invention as applied to sulfid ores, it will be apparent to those skilled in the art that it may be advantageously employed in many other ways. I do not, therefore, wish to limit myself to the precise disclosure herein set forth; but,

Having thus described my invention, I claim as new and desire to secure by Letters Patent—

1. The herein-described process of treating zinc ores containing cadmium sulfid and zinc sulfid, which consists in subjecting ore to a dead roast, whereby the zinc sulfid is oxidized and the cadmium sulfid converted into cadmium sulfate, thereafter dissolving out this deleterious sulfate and then grinding and distilling the remaining zinc oxid to obtain therefrom the pure refined zinc.

2. The herein-described process of treating zinc ores containing cadmium sulfid and zinc sulfid, which consists in subjecting the ore to a dead roast, whereby the zinc sulfid is oxidized and the cadmium sulfid converted into cadmium sulfate, thereafter treating the ore with water to dissolve out this deleterious sulfate and then grinding and distilling the remaining zinc oxid to obtain therefrom the pure refined zinc.

In witness whereof I hereunto subscribe my name this 3d day of June, A. D. 1902.

PHILIP A. MACKAY.

Witnesses:

DAISY WESTON,

J. W. KRUGER.