T. HUNTINGTON & F. HEBERLEIN.
PROCESS OF RECOVERING ZINC AND OTHER VOLATILE METALS.
APPLICATION FILED OCT. 25, 1910.
1,069,085. Patented July 29, 1913.

WITNESSES:
Minerva Gold
Alice Bell

INVENTORS.
Thomas Huntington
& Ferdinand Heberlein

BY
Penne & Gildnreth
ATTORNEYS.
To all whom it may concern:

Be it known that we, THOMAS HUNTINGTON, metallurgist, a citizen of the United States of America, residing at 3 Lombard Street, London, England, and FERDINAND HEBERLEIN, metallurgist, a subject of the Emperor of Germany, and residing at 55 Savignystrasse, Frankfort-on-the-Main, Germany, have invented certain new and useful Improvements in Processes of Recovering Zinc and other Volatile Metals, of which the following is a full and exact specification.

Owing to the deficiencies of the processes in general use up to now for the distillation of zinc ores in muffle furnaces, efforts have been made with a view of carrying out the zinc distillation in shaft "blast" furnaces, but all such trials have been unsuccessful. The failures are mainly due to the working of the blast furnace itself. Owing to the complete liquefaction of the slag and to the continuity of the process, it is found impossible to keep the escaping gases sufficiently free from oxygen contained in the air blast and also from other oxidizing gases, (carbon dioxide, CO₂, and the like), the presence of such oxidizing gases making it impossible to obtain the zinc vapors free from oxid and to then condense them into a compact metal. It is for these reasons that thus far only zinc oxide or zinc dust containing a high percentage of zinc oxide have been obtained in blast furnaces.

The present invention has for its object the solving of the problem of recovering zinc in a compact metallic form by means of a process in which air is blown through the mass of ore.

The invention is based on a well known process, the object of which is to volatilize the zinc and to recover it in the form of zinc oxide. This known process consists in mixing zinc ores or zinciferous products in a pulverulent or granular form with fine coal or other fuel when not already contained therein, as for instance in the case of muffle residues. The mixture is then fed into a suitable furnace, such as for instance the Huntington-Heberlein converter furnace, and after starting ignition, submitting it to the action of a current of air traversing the layer of material under treatment from below up to the surface of the charge.

Owing to the phenomena of combustion, reduction and oxidation which take place, the zinc is volatilized and carried along in the form of oxid together with the escaping combustion gases and is then recovered by means of suitable filtering devices or the like.

In the process just described, as well as in other similar volatilization processes where the air current is directed from below to the top, the intention and result was always to recover the zinc in form of oxid. The method was either to employ a relatively thin layer of material in connection with a relatively low air pressure or a relatively thick layer with a relatively high air pressure. In both cases the gases always contained oxygen and other oxidizing gases (carbon dioxide and the like) in excess and the nascent zinc vapors thereof were converted into oxid. In all these known processes it is neither intended nor is it possible to recover the zinc in a liquid metallic form, because the presence of an excess of oxygen and other oxidizing gases is thereby inevitable.

Now according to the present invention this known and discontinuous air blowing process is modified in such a way that the air and gas current is not directed from below to the top but reversed, namely from the surface of the charge through it to the bottom, the layer of charge being comparatively thick. In the course of trials carried out with these new methods, the startling result was observed, that oxidation of the zinc vapors can be avoided, so that these vapors on leaving the charge may be almost completely condensed and liquefied by suitable means and thus be recovered in a compact metallic state.

In the accompanying drawing illustrating a furnace adapted for performing the process in accordance with our invention a is a 105 converter furnace filled with the charge c resting on the perforated grate f, while d is a cover tightly secured upon the converter and provided with an air inlet b. The outlet for the gases and vapors is at g. The
converter can be tilted over by turning the trunnions on which it is supported. The process may be carried out for instance as follows: The zinciferous ore or zinc products mixed with fuel is fed in a comparatively thick layer into a converter furnace. On the surface of the charge an ignition fire is started and through the air-tight converter-hood a current of air is admitted.

First a combustion of the fuel will take place in the upper part of the layer, and owing to the increase of temperature thereby caused, and also owing to the reaction of the ore-particles with the carbon present in the mixture and the carbon monoxid developed by the combustion, the zinc will be reduced in this upper layer and will pass vertically downward in form of metallic vapor together with the gas current. The gases coming from the upper layers will gradually preheat the mixture of ore and coal below. After some time, the whole fuel of the upper layer will be burned out bringing the temperature in this layer to such a degree, that the mass is almost avoiding the mean time, the zinc from this upper layer has distilled out, the completeness of its removal being considerably furthered by the close contact existing in the moment of sintering between the coals still present in the charge, and the ore particles. Through the sintered upper layer which is screen-like interspersed with air-channels, the fresh air current is passing and reaches the lower unsintered layer, which still contains the bulk of its fuel-contents. The same phenomenon as in the uppermost layer will now take place here, i. e. the fuel will be burned by the oxygen of the air and the zinc volatilized, until finally the sintering of the whole mass is accomplished. These phenomena will continue downward from one layer to the other, until the sintering zone has reached the bottom part of the charge, when the process is finished. The gases and metal vapors escaping from the layer which is near the sintering state, pass through the layers lying beneath until they escape at the bottom of the charge. Thus the gases will preheat these layers of charge and prepare them, by reducing and decomposing the oxides, carbonates, sulfates and like compounds contained in the charge and injurious to the subsequent production of metallic zinc vapors. On the other hand, oxidizing constituents of the gases will be reduced in passing through the still unsintered layers of the charge intermingled with live coal, so that on leaving the charge at the bottom, the gases essentially consist of only carbon monoxid (CO) and nitrogen. The zinc vapors mixed with the gases will first be partly oxidized and retained in the charge in the form of zinc oxide, and partly condensed to a metallic state in the inferior cooler layers of the charge. During a certain preliminary stage of the operation, which according to the prevailing conditions will be shorter or longer, no zinc vapors will thus escape from the lower part of the charge, but only the gases developed by the combustion of the carbon and the decomposition of the carbonates, sulfates, etc.; as soon however a sufficiently high temperature is reached also in the lower layers of the charge, the principal stage of the process begins, during which also the zinc vapors will escape and may be condensed after having left the charge, by suitable means, for instance by causing the gases to pass over cooled surfaces. Owing to the working of the charge in the preliminary stage and also to the reduction of the carbonic dioxid (CO₂) contained in the gases, by the incandescent coal of the charge, the gases are absolutely clean, and consist essentially of only monoxid of carbon and nitrogen, the condensation of the zinc vapors to liquid (or solid) metallic zinc is obtained without difficulty and the formation of zinc dust and zinc oxide avoided. The astonishing phenomenon is, that in the process described the zinc does not escape from the charge in the form of zinc oxide, but mainly in the form of metallic zinc vapors, capable of being condensed to liquid metallic zinc, whereas in the hitherto known analogous processes and in the known blast furnace work, only zinc oxide could be obtained, or under most favorable circumstances an inferior quality of zinc dust. This is most probably due to the following reasons: When in the process, where an air current passes through the charge sintering the same, and the current is directed from the bottom to the top, it is not possible to obtain a uniform distribution of the air over the whole area of the charge. In consequence of their tendency to expand, the gases are seeking a passage through the charge at those points, which offer the least resistance. Thus crater-like channels will be formed in some parts of the charge and through these channels the air reaches the surface of the charge in a more or less unaltered condition, mixing there with the gases and vapors escaping from the charge. In addition, this crater-formation causes an irregular combustion and sintering to take place, so that the sintering does not propagate upwardly by uniform layers, but irregularly with respect to the horizontal and vertical section of the mass. Furthermore, the above-mentioned preparatory preheating and reduction is prevented and there are many parts of the mass in which the volatilization of the zinc is taking place simultaneously with the reduction of the above-mentioned injurious oxides, sulfates, carbonates, and like compounds, with the result that the gases holding the zinc vapors also carry along the carbon monoxid and the ox-
dizing elements (carbon dioxide, etc.) generated by the reduction of the oxides, sulfates, carbonates, etc., whereby the zinc vapors are converted to oxide. The word oxidizing is used here in the sense that the elements generated by the reduction of oxides, sulfates, carbonates, and like compounds exert an oxidizing action upon the zinc vapors. If however according to the present invention, the gas and air current is directed from the surface of the charge downward, and if a relatively high layer of charge used, the expansion of the gas current is counteracted by the fact of the resistance offered by the charge to the passage of the gases which increases toward the bottom in consequence of the greater density of the lower layers of the charge. And this will have for effect that the gas current is distributed uniformly over the whole area of the charge and crater-like formations are avoided, hence a uniform preparation of the charge and a uniform propagation of the sintering toward the bottom. Under this arrangement it is possible to have the escaping gases contain only carbon monoxid and vapors of metallic zinc.

From the foregoing it is obvious that the success of the invention depends upon using relatively thick layers of charge, a "relatively thick layer" meaning a height of for instance 100 centimeters. If the layer is too thin, there will be no preparatory reduction and decomposition of the oxides, sulfates, carbonates, etc., nor will the gases be cleaned from oxidizing constituents, which according to the above explanations, is indispensable for obtaining condensable metallic zinc vapors. The height of layer required for each case however depends upon the percentage of zinc and the nature of the material to be treated, and must be established for each material by practical experience. It is evident that the pressure and quantity of the air passing through the mass must be proportionate, that is to say adapted to the height of layer employed and other prevailing circumstances. Pure oxygen or air enriched in oxygen or preheated air or oxygen may of course be employed instead of air.

In working the process practically, it was found that it was difficult to distil the zinc out of the lower layers of the charge in a metallic form, which difficulty may be explained by the fact that the bottom layer of the charge does not exert a sufficient reducing action upon the combustion gases and zinc vapors prior to their escape from the charge. To avoid this difficulty it is advisable to add in the bottom layer of the charge a larger quantity of reducing fuel than in the rest of the charge. Owing to this increase of reducing fuel in the lower layer, the danger of reoxidation of the zinc vapors is lessened and it is possible to distil the zinc in metallic form also out of the lower layers of the charge. It might be advisable to have no ore at all in the bottom layer of the furnace, but to allow the charge to rest upon a layer of reducing fuel (preferably coke). This reducing bottom layer might serve as a grate, by putting for instance on the bottom of the furnace first a layer of coarse coke, and upon this a layer of finer coke, upon which the charge itself is fed. It might also be advisable to separate the charge into several layers and provide a layer of charge richer in fuel (or of fuel only) between two such layers. The arrangement of layers of higher reducing capacity between or underneath the charge may have another favorable effect, inasmuch as these layers secure, during the whole operation, a more perfect reduction of the oxidizing constituents of the gases and of the already generated metallic oxide.

From the process of distilling zinc in blast furnaces, which never has been successful, the present process differs substantially in that (1) in the present process the slag is not converted into a fluid state, but only sintered; (2) the present process is not carried out continuously, but discontinuously, i.e. in each operation a determined quantity of charge is submitted to distillation and when completed the work begins once again. As in the well-known blast-furnace distillation the zone at which the slag is liquified must nearly coincide with the zone at which the generation and distillation of the zinc takes place, it is inevitable that part of the air blown in or the carbon dioxide generated by the combustion, reaches the zinc distillation zone and thereby reoxidizes the zinc vapors. Moreover, in the blast furnace work, there is not sufficient preparation of the charge, i.e. injurious oxides, carbonates, sulfates, etc., are not sufficiently reduced and decomposed before zinc reduction is taking place and because in blast furnace the layers are naturally charged loosely, the gases traverse them quickly and without the necessary close contact with the particles of the charge.

The startling result obtained by the present invention, in recovering in a metallic state the zinc vapors on their leaving the charge, may partly be ascribed to the fact that the charge forms a densely stratified mass, the mass of material being a pulverulent or granular state, or when in form of briquets, the spaces between the briquets must be completely filled in with fine coal or fine charge material. The thus obtained density of the charge will further the uniformity of the gas distribution, and a more intimate contact of the gases with the particles of the charge, and also will slacken the passage of the gas current through the mass of the charge, whereby a uniform and
The trials on which the present invention is based, were carried out in a converter furnace, such as is made use of in the Huntington-Heberlein process for roasting lead ores. The converter, and consequently the charge contained therein, was tapered toward the bottom and it appears that this tapering form of the charge is of a certain importance for the success of the invention, especially for the purpose of producing clean metallic zinc vapors. Because in consequence of this downward tapered section of the charge, the uniformity of the gas distribution is furthered, and the crater formation counteracted, a better preparation of the charge is secured and a better cleaning of the gases, inasmuch as the downward passing gases are coming into more intimate contact with the charge in the lower reduced section of the furnace. Furthermore it has been found in the practical working of the invention, that a certain amount of water or other vaporizable liquid in the charge exerts a favorable influence upon the course of the process. It would seem that owing to such water contents the preliminary period, during which the charge is being gradually brought to the volatilization temperature of the zinc, and prepared in other respects, is extended, and that in the mass of the charge a system of fine channels is formed by the escaping water vapors. The volatilization temperature is thereby distributed with greater uniformity over the whole mass of the charge. Moreover, the favorable effect of the water is perhaps due to certain chemical reactions of the water (formation of hydrogen, decomposition of injurious compounds, etc.).

In comparison with the present zinc distillation processes in muffle furnaces, the present process has the advantage of much greater cheapness and very simplified working. Moreover the new process can be worked with profit on materials poor in zinc, such as for instance in the case of re-tort residues and ore-tailings, low grade zinc ores and the like. A further advantage of the present invention consists in the fact that the zinc recovery is a good one. Doubtless this advantage is also due to the uniform distribution of the gases and the uniform progress of the sintering.

It is obvious that the present process is not necessarily confined to the production of metallic zinc. In making use of the methods characterizing the process, zinc or other volatile metals from ores or other materials, which consists in charging a comparatively thick layer of the ore or other material mixed with reducing fuel in a suitably arranged furnace, igniting the charge at the top, forcing an air current downward through the charge, thereby generating within the body of the charge the combustion gases and distilling the volatile metals out of the charge, condensing the metallic vapors, reducing the oxidizing constituents of the gas current by the incandescent fuel, distilling the volatile metals out of the charge, condensing the metallic vapors, sintering substantially the entire residues and discharging the sintered mass for preparing the furnace to receive a fresh charge.

The invention is not only applicable to zinc, but also to other volatileizable metals, especially lead, arsenic, antimony, tin and mercury.

The method herein disclosed also lends itself to the separate recovery of several metals contained together in ore or metalurgical products. As a result of the comparatively uniform progress during the process and the comparatively uniform increase in temperature occurring progressively throughout the lower portions of the charge, the metal having the lowest temperature of volatilization first passes from the furnace as a vapor, and then the metal having the next higher temperature of volatilization passes from the furnace, and so on. If, for instance, zinc and lead are mixed together in the charge, substantially all the zinc vapor escapes first, and then, after the bulk of zinc is volatilized, the lead vapor starts to pass from the furnace, so that the two may be recovered separately, as, for example, by directing the zinc vapors into one place and then diverting the following vapors into another place at the time that the lead starts to volatilize; or, as an alternative to the procedure in this example, the air current may be shut off and the process terminated after the volatilization of the zinc is completed. The residue from which the zinc content has been extracted then remaining in the furnace, may be treated in a blast furnace for recovering the lead content. Easily volatilized metals, such as arsenic, antimony, mercury, already escape prior to the volatilization of the zinc and may also be recovered separately if desired.

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

1. The process of recovering zinc and other volatile metals from ores or other materials, which consists in charging a comparatively thick layer of the ore or other material mixed with reducing fuel in a suitably arranged furnace, igniting the charge at the top, forcing an air current downward through the charge, thereby generating within the body of the charge the combustion gases and the volatile metals, reducing the oxidizing constituents of the gas current by the incandescent fuel, distilling the volatile metals out of the charge, condensing the metallic vapors, reducing the oxidizing constituents of the gas current by the incandescent fuel, distilling the volatile metals out of the charge, condensing the metallic vapors, sintering substantially the entire residues and discharging the sintered mass for preparing the furnace to receive a fresh charge.

2. The process for recovering zinc and other volatile metals from ores or other materials, which consists in charging a com-
paratively thick layer of the ore or other material mixed with fuel into a suitable furnace, said layer being tapered toward the bottom, igniting the charge at the top, forcing an air current downward through the mass, decomposing and reducing by the downward escaping combustion gases the compounds of the charge which may be injurious to the subsequent production of metallic vapors, reducing the oxidizing constituents of the gas current by the incandescent fuel, distilling the volatile metals out of the charge, condensing the metallic vapors, sintering the residues and discharging them for preparing the furnace to receive a fresh charge.

3. The process of recovering zinc and other volatile metals from ores or other materials, which consists in charging a comparatively thick layer of the ore or other material mixed with reducing fuel and moistened with a vaporizable liquid, into a suitable furnace, igniting the charge at the top, forcing an air current downward through the charge, decomposing and reducing by the downward escaping combustion gases the compounds of the charge which may be injurious to the subsequent production of metallic vapors, reducing the oxidizing constituents of the gas current by the incandescent fuel, distilling the volatile metals out of the charge, condensing the metallic vapors, sintering the residues and discharging them for preparing the furnace to receive a fresh charge.

4. The process of recovering zinc and other volatile metals from ores or other materials, which consists in charging a comparatively thick layer of the ore or other material mixed with reducing fuel into a suitable furnace and upon layers of increased reducing power, igniting the charge at the top, forming an air current downward through the charge, decomposing and reducing by the downward escaping combustion gases the compounds of the charge which may be injurious to the subsequent production of metallic vapors, reducing the oxidizing constituents of the gas current by the incandescent fuel, distilling the volatile metals out of the charge, condensing the metallic vapors, sintering the residues and discharging them for preparing the furnace to receive a fresh charge.

5. The process of recovering zinc and other volatile metals from ores or other materials, which consists in charging a comparatively thick layer of the ore or other material mixed with reducing fuel into a suitable furnace and upon layers of fuel, igniting the charge at the top, forcing an air current downward through the charge, decomposing and reducing by the downward escaping combustion gases the compounds of the charge which may be injurious to the subsequent production of metallic vapors, reducing the oxidizing constituents of the gas current by the incandescent fuel, distilling the volatile metals out of the charge, condensing the metallic vapors, sintering the residues and discharging them for preparing the furnace to receive a fresh charge.

6. The process of recovering zinc and other volatile metals from ores or other materials, which consists in charging a comparatively thick layer of the ore or other material mixed with fuel and moistened with water, into a converter furnace tapered toward the bottom, and upon layers of increased reducing power, igniting the charge at the top, forcing an air current downward through the charge, decomposing and reducing by the downward escaping gases of combustion the compounds of the charge which may be injurious to the subsequent production of metallic vapors, reducing the oxidizing constituents of the gas current by the incandescent fuel, distilling the volatile metals out of the charge, condensing the metallic vapors by means of cooled surfaces, sintering the residues and discharging them for preparing the furnace to receive a fresh charge.

7. The process of treating ores or other materials containing zinc and other volatile metals, which consists in charging a comparatively thick layer of the ore or other material mixed with fuel into a suitable furnace, igniting the charge at the top, forcing an air current downward through the charge, decomposing and reducing by the downward escaping combustion gases the compounds of the charge which may be injurious to the subsequent production of metallic vapors, reducing the oxidizing constituents of the gas current by the incandescent fuel, distilling the volatile metals out of the charge, burning the metallic vapors to oxid after they have left the charge, sintering substantially the entire residues and discharging the sintered mass for preparing the furnace to receive a fresh charge.

8. The process of recovering zinc and other volatile metals from ores or other materials, which consists in charging a comparatively thick layer of the ore or other material mixed with fuel into a suitable furnace, igniting the charge at the top, forcing an air current downward through the charge, decomposing and reducing by the downward escaping combustion gases the compounds of the charge which may be injurious to the subsequent production of metallic vapors, reducing the oxidizing constituents of the gas current by the incandescent fuel, distilling one or more of the volatile metals out of the charge and leaving behind in the residues the other less volatile metals, condensing the metallic vapors, sintering substantially the entire residues and
9. The process of recovering zinc and other volatile metals from ores or other materials, which consists in charging a comparatively thick layer of the ore or other material mixed with fuel into a suitable furnace, igniting the charge at the top, forcing an air current downward through the charge, decomposing and reducing by the downward escaping combustion gases and the compounds of the charge which may be injurious to the subsequent production of metallic vapors, reducing the oxidizing constituents of the gas current by the incandescent fuel, distilling the volatile metals one after the other out of the charge, condensing separately the different metallic vapors, sintering the residues and discharging them for preparing the furnace to receive a fresh charge.

In testimony whereof we have signed our names to this specification in the presence of two subscribing witnesses.

THOMAS HUNTINGTON.
FERDINAND HEBERLEIN.

Witnesses:
JEAN GRUND,
CARL GRUND.

Copies of this patent may be obtained for five cents each, by addressing the "Commissioner of Patents,
Washington, D.C."

It is hereby certified that in Letters Patent No. 1,069,085, granted July 29, 1913, upon the application of Thomas Huntington, of London, England, and Ferdinand Heberlein, of Frankfort-on-the-Main, Germany, for an improvement in "Processes of Recovering Zinc and other Volatile Metals," an error appears in the printed specification requiring correction as follows: Page 5, line 48, for the word "forming" read "forcing; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 7th day of October, A. D., 1913.

R. T. FRAZIER,
Acting Commissioner of Patents.
discharging the sintered mass for preparing the furnace to receive a fresh charge. 9. The process of recovering zinc and other volatile metals from ores or other materials, which consists in charging a comparatively thick layer of the ore or other material mixed with fuel into a suitable furnace, igniting the charge at the top, forcing an air current downward through the charge, decomposing and reducing by the downward escaping combustion gases and the compounds of the charge which may be injurious to the subsequent production of metallic vapors, reducing the oxidizing constituents of the gas current by the incandescent fuel, distilling the volatile metals one after the other out of the charge, condensing separately the different metallic vapors, sintering the residues and discharging them for preparing the furnace to receive a fresh charge.

In testimony whereof we have signed our names to this specification in the presence of two subscribing witnesses.

THOMAS HUNTINGTON.
FERDINAND HEBERLEIN.

Witnesses:
JEAN GRUND,
CARL GRUND.

Copies of this patent may be obtained for five cents each, by addressing the “Commissioner of Patents, Washington, D. C.”

It is hereby certified that in Letters Patent No. 1,069,085, granted July 29, 1913, upon the application of Thomas Huntington, of London, England, and Ferdinand Heberlein, of Frankfort-on-the-Main, Germany, for an improvement in “Processes of Recovering Zinc and other Volatile Metals,” an error appears in the printed specification requiring correction as follows: Page 5, line 48, for the word “forming” read forcing; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 7th day of October, A. D., 1913.

[Seal.]

R. T. FRAZIER,
Acting Commissioner of Patents.