C. V. THIERRY.

METALLURGY OF ZINC.

APPLICATION FILED OCT. 6, 1911.

1,030,350.

Patented June 25, 1912

3 SHEETS—SHEET 1.

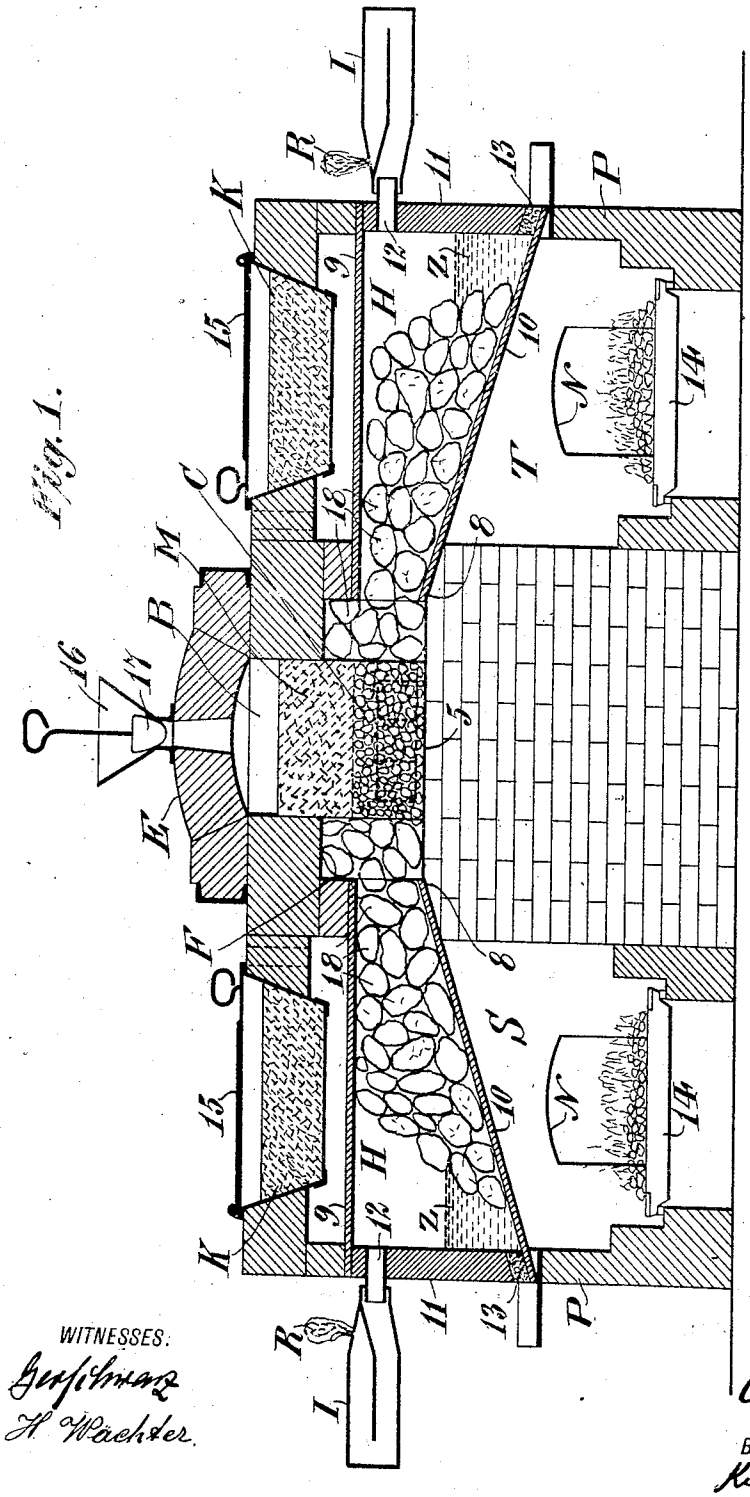

Fig. 1.

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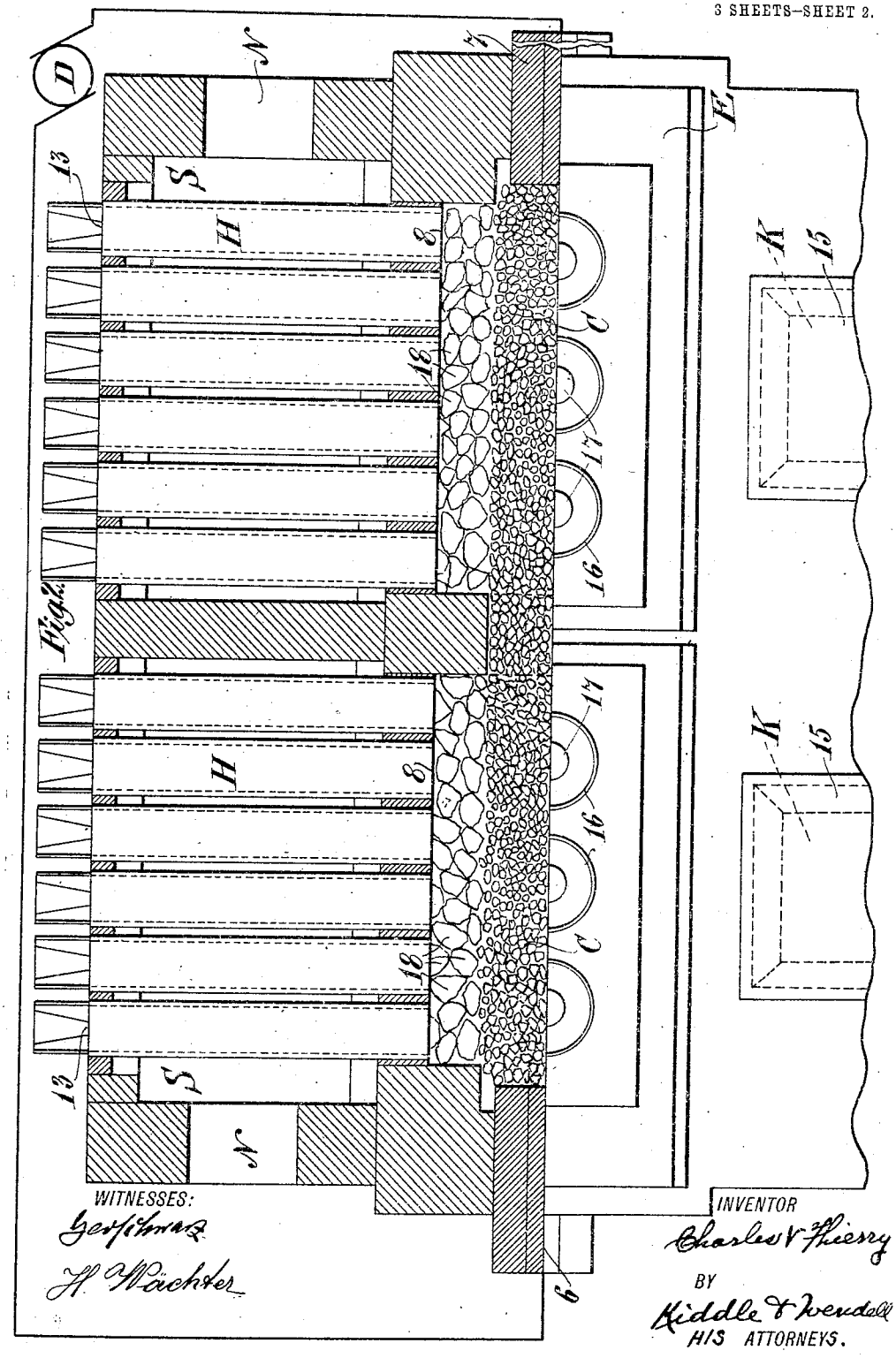

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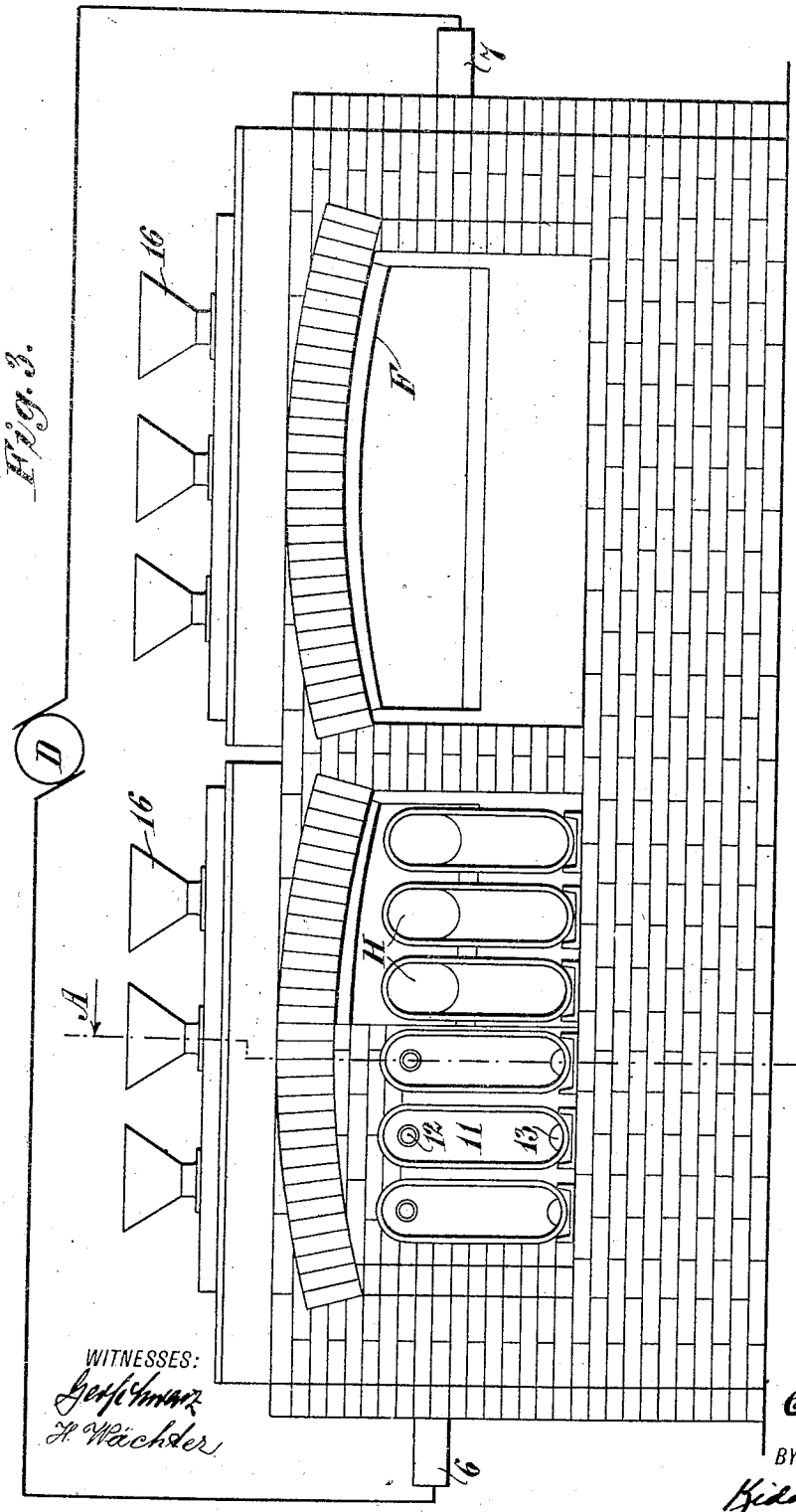

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METALLURGY OF ZINC.

1,030,350. Specification of Letters Patent. Patented June 25, 1912.

Application filed October 6, 1911. Serial No. 653,249.

To all whom it may concern:

Be it known that I, CHARLES V. THIERRY, a citizen of the Republic of France, and a resident of the city of Paris, in said Republic of France, have invented certain new and useful Improvements Relating to the Metallurgy of Zinc, of which the following is a specification.

This invention relates to the metallurgy of zinc and the object thereof is to produce metallic zinc by the reduction of oxid-of-zinc (ZnO) by carbon (C); the heat necessary for such decomposition being derived from an electric current passed through a "resistor" in the form of a bed of broken carbon.

The invention also relates to the manufacture of zinc from the oxid-of-zinc by reducing the oxid by and in the presence of heated carbon, thereby producing fumes of zinc, and subsequently condensing said fumes to liquid zinc by retaining the fumes in the presence of carbon until the zinc fumes have been condensed.

The invention furthermore relates to apparatus particularly adapted for and designed to accomplish the above in a practical, effective and commercial manner.

In general terms, the resistor, above referred to, is comprised in a bed of carbon, usually made of coke, loosely disposed upon a refractory hearth and confined by side-walls, the inner half of which is preferably of the same material, *i. e.*, carbon. The size and shape of the carbon pieces in the resistor as well as the depth, width and length of the resistor bed may be variously modified to obtain any electrical resistance and intensity of current which may be desired; but the pieces ordinarily used are from about $\frac{3}{8}$ to $\frac{3}{4}$ inch diameter. The current is brought to the two ends of the resistor by blocks or rods of amorphous carbon or graphite which pass through suitably tamped joints in the end-walls of the furnace, that is the resistor is interpolated between the two terminals. It will be evident that the refractory material used in the construction of the chamber or channel that contains the resistor should be a poor conductor of electricity, whereby to avoid current leakage and useless dissipation of energy. The reaction and resistor chamber of the furnace is made of sufficient depth to also receive the charge; which is placed directly upon and is sustained by the resistor.

The charge in its entirety is either a mixture or alternate layers of oxid-of-zinc and of carbon in preferably the exact relative proportions to effect, when suitably heated, their complete reduction.

As has already been intimated, the electric energy is transformed into caloric energy in the resistor-bed; the heat thus generated effects the decomposition of the superimposed mass and the following chemical reaction ensues:

$$ZnO+C=Zn+CO.$$

As a consequence of the foregoing conditions, the charged material is evolved in gaseous forms. Thus, on the one hand, fumes-of-zinc, and, on the other hand, oxid-of-carbon, are produced. The zinc-fumes, together with the oxid-of-carbon, or any other entrained gases, escape through a suitable opening, or openings, in the furnace walls into a condenser, or condensers, where the zinc fumes (Zn) condense in a metallic form and the oxid-of-carbon (CO) mingles with the atmosphere or is burned.

To obtain zinc as a fluid metal, it is essential that the condenser, or condensers, shall be maintained by some suitable method and means at the proper thermal conditions. In fact, the temperature of a condenser should progressively decrease, from the entry-end to the other, falling from about 950° to 450° C.; but no portion of a condenser should be lower than somewhat above the temperature of the melting point of zinc, or say about 420° C. as a minimum. This condition may be effectually obtained by control of the radiated heat and also by externally heating the condenser. Again, to avoid a secondary oxidization of the zinc-fumes, as by such gases as CO_2, H_2O, etc., they should be kept continuously in a reducing medium: the gases escaping from the furnace should, as it were, be filtered and the condensing surface be as great as possible.

An example or embodiment of my invention is shown in the accompanying drawings in which,

Figure 1 is a vertical transverse section of the furnace and its condensers, as on the line A of Fig. 3; Fig. 2 is a horizontal section to the longitudinal center line, the re-

mainder, partially broken off, being in plan, and Fig. 3 is a side elevation, a series of the condensers being omitted on the right hand side to show the aperture in the furnace wall into which the "necks" of the condensers are cemented.

B is the reaction chamber on whose bottom, or hearth 5, is placed the bed of carbon which constitutes the "resistor" C, its ends being in contact with the terminals or electrodes, 6, 7, which convey the current to the resistor, as from the power circuit D. The chamber is closed by a cover, or covers, E. Openings, as F, are formed in the side walls of the chamber, which receive the inlet ends, 8, of the condensers, as H. The condensers as here shown are of trapezoidal form in vertical longitudinal section; the upper portion, 9, being set horizontal so as to give a suitable slope on the lower surface, 10, for the flow of the condensed zinc. The smaller, or inlet, ends of the condensers are set and secured into the furnace openings F by a tamped joint, but their faces only penetrate to about the middle of the thickness of the furnace walls or to the point where the carbon portions of the side walls begin. The large, or outer, ends of the condensers are closed by plugs of refractory material, as 11, having a vent, 12, for the escape of CO, while the tap hole, 13, at the bottom, is for drawing off zinc.

If it is desired to make "blue-powder", then the ordinary "balloons", as I, are connected to the vent-openings, 12, in which instance the CO and other fixed gases pass therein and therethrough and are burned as shown at R.

In the present illustration, there are four furnace openings, F, each adapted to receive six condensers, that is twelve on each side, or twenty-four in all. The condensers are inclosed in chambers, S, T, formed of brick work, and under each series of condensers is a grate 14, upon which charcoal, coke or coal may be burned, when required, to increase the temperature within the chambers. Naturally, this heating may be obtained in any other appropriate manner, as by means of gas or a resistor acted upon electrically.

Receptacles, as K, may be placed in the top or roof of the condenser chambers, whereby to receive the oxid-of-zinc, or a mixture of the oxid and carbon, for the purpose of pre-heating the same by utilization of a portion of the heat radiated by the condensers or generated by the grate-fire. These receptacles may be conveniently inclosed, as by the covers 15. The furnace cover is provided with a series of openings, disposed above the reaction chamber, in which are placed feed-funnels, 16, ordinarily closed by means of plugs, as 17.

In the primary assemblage of the furnace, the longitudinal portions in front of the openings F, of the inner ends of the condensers, and also the interiors of the condensers themselves, are packed with large pieces of carbon, as 18, and the carbon for forming the resistor-bed is then placed in the channel, resting upon the bottom, or hearth, of the chamber. The packs of carbon which are located upon the opposite sides of the furnace in the longitudinal portions above referred to, really constitute and form the inner halves of, or at least the linings for, the side walls of the furnace.

The operation of the furnace is as follows:—The resistor preferably having been brought by the passage of electric current to the desired temperature, say about 1200° to 1300° C., a composite charge of oxid-of-zinc and of carbon, as M, is applied directly upon the upper surface of the resistor. It should be noted however that the chamber may be charged before switching on the current or when the resistor is only partially heated. The thickness or depth of the charge should be sufficient to prevent the zinc fumes and oxid-of-carbon from passing up therethrough. This also avoids excessive radiation of heat from the top of the charge. On the other hand, the charge should not be so deep and heavy as to sensibly diminish, by its pressure and conductivity, the electrical resistance of the underlying resistor.

The reaction

$$ZnO+C=Zn+CO,$$

takes place principally where the charged mixture impinges upon the resistor. The zone of reaction, however, extends somewhat upwardly into the charge and also perhaps along the sides of the resistor, that is somewhat in the carbon packed within the aforesaid furnace-chamber spaces or in the carbon forming the inner portions of the side walls. But the height of the reaction within the mixture of oxid and carbon is maintained practically constant by successive rechargings, the frequency and quantity of which depend upon the rapidity of the reaction.

However anomalous it may appear as related to a zinc furnace, it is yet a matter of fact that, when a fairly constant depth of charge is maintained, the furnace may be operated without covering the reaction chamber. Nevertheless, the presence of a cover is preferable and has a distinct utility when it is desired to visually examine the reaction chamber and to expose the upper surface of the resistor, as before this can be done the charge must be allowed to completely exhaust itself.

The funnels in the cover provide a convenient means of charging and also, by rods or bars, to spread the same if necessary. Moreover, they can be utilized as peep-holes.

However, the feeding intervals are best denoted by a volt-meter; for when a charge is approaching exhaustion this sufficiently affects the normal resistance to serve as an indication that additional material is required.

It will now be seen that the fumes and gases produced by the reaction can only escape into the condensers by passing down into and out, sidewise, from the resistor itself; thence through the packed carbon in the sides and finally into the interstitial spaces formed by the carbon contained within the condensers. Consequently, from the instant when the zinc is gaseously evolved until precipitated as liquid metal it must necessarily and continuously flow in a path obstructed by a reducing medium.

The condensing zone begins at, or near to, the inlets of the condensers and this zone continues outwardly, but with a progressively decreasing temperature, until the liquid zinc Z, is collected at the front ends, along the lower surfaces, as indicated.

In first putting the furnace into operation it is advantageous to pre-heat the condensers to a proper temperature, which is well attained by means of the fuel-fired grates, 14. Then by constructing the outer walls, as P, of the condenser chambers comparatively thin, whereby to realize a rapid and free radiation of heat from the ends of the condensers farthest from the furnace, it becomes an easy matter, by manipulation of the fire, and also of the stoke-openings, as N, to prevent the temperature from becoming either too high or too low.

There is an advantage of considerable practical importance in having the condensers in parallel batteries on the right and left hand sides of the furnace; which consists in the ability to draw off the molten zinc successively from one condenser after another and without suspending or materially diminishing the rate of the reaction.

It is to be particularly noted that in the present system the evolution of the zinc fumes will proceed according to the rapidity with which heat units are supplied to the resistor: and by a proper control of the in-put of energy the temperature of the evolved fumes and gases needs be but comparatively little higher than that required to produce the reaction. Therefore, as an ample temperature for the purpose is about 1300° C., ordinary fire bricks may be used in the construction of the reaction chamber which, under such conditions, will endure indefinitely, as has been thoroughly proven in actual practice.

Obviously, as respects the charge, the ideal materials and condition would be chemically pure oxids-of-zinc (ZnO) and carbon (C) combined in the precise relative proportions to produce a complete reaction, whereby all of the materials would be evolved in the gaseous forms of zinc (Zn) and oxid-of-carbon (CO). Hence, there would be no residue whatever, and so far as is known, the furnace might thus operate continuously for months, or even years. But, in actual practice, the use of materials of theoretical purity would probably be commercially prohibitive and their precise proportionment in successive charges might be troublesome to realize. However, perfect conditions are not necessary to gain the advantages of this invention; for with oxid-of-zinc and carbon (coke) of ordinary commercial grade or quality then the actual residue—chiefly in the form of sintered ash—is a relatively negligible quantity over the period of operation (weeks or months) which is attainable; and even then the removal of a resistor-bed with any collected residue, and the substitution of a new resistor, involves but a trifling delay and expense. Again, it matters little whether the two constituents of the charge are fed to the furnace in precisely exact proportions; for if there should be, on the one hand, an excess of oxid-of-zinc, this will make itself apparent by "eating up" carbon from the resistor and will be denoted by a change in the electric resistance; the remedy for this would be to charge relatively more carbon. On the other hand, if an excess of carbon is accumulated in the reaction chamber, this will also make itself known by a change in the normal resistance: the remedy for this would be to insert relatively more oxid-of-zinc.

The exclusion of air from the reaction zone of the furnace chamber may be said to be absolute. Even the oxygen which may be entrained and carried in with the charge is expelled and passes out of the reaction chamber through the feed openings in the cover before it can reach the reaction zone. This is also the case as to moisture and applies more or less to other volatilizable substances. Consequently, the difficulties of condensation are by so much diminished and the carbon of the resistor and the terminals are neither deteriorated nor consumed.

The determining factor which limits the capacity of the herein described furnace is, taken as a whole, the condenser. Hence, as a glance at the drawings will show, the effort has been to supply a condensing system which shall have a high rate of output. Yet it is feasible to still further amplify this element, as by the use of deeper and longer condenser-tubes and also, say, by superimposing one set of condensers above another.

By this system it has been demonstrated in a furnace continuously operating for weeks, and delivering zinc at the rate of about seventy-five pounds an hour, that either liquid zinc entirely, or a combination

of both liquid zinc and "blue-powder," may be obtained at will. To produce "blue-powder" it is simply necessary to attach "balloons" to the condensers and somewhat increase the in-put of energy, thereby evolving zinc fumes more rapidly than the condensers can precipitate them in the form of liquid metal; hence the volume of zinc-fumes in excess of the liquid condensing capacity is blown into the external metallic receivers and is regained as dust. On the other hand, to avoid the production of "blue-powder," and yet run the furnace at a high rate of reaction, one requires only to diminish the electric energy until a balance with the condenser is established.

The various operations are not onerous or difficult and can be satisfactorily performed, as has been proven, by unskilled labor. Moreover, by suitably timing the periods of charging and tapping, a single gang can readily manipulate a considerable number of furnace-units.

I claim as my invention:—

1. In the metallurgy of zinc, the placing and maintaining of a composite charge of commercially pure oxid of zinc and of carbon directly upon a separate carbon resistor of an electric furnace, from which air is excluded, the relative proportions of the charged materials being such that when a sufficient current is passed through the resistor to produce reaction in the superimposed oxid of zinc and the carbon they will be completely transmuted into fumes, gases, vapors and an inert ashy or sintered residue; the volatilized products automatically passing from the reducing zone, as and when produced, but the residue remaining upon in or beneath the resistor until otherwise removed.

2. In the metallurgy of zinc, the placing and maintaining of a composite charge of commercially pure oxid of zinc and of carbon directly upon a separate carbon resistor of an electric furnace, from which air is excluded, passing a current through the resistor to produce reaction in the charged materials and from time to time increasing or decreasing the separate elements of the charged materials whereby their averaged relative proportions will be such that they will be entirely transmuted into volatilized products and a modicum of inert ashy or sintered residue, the volatilized elements escaping, as and when produced, but the residue remaining at the resistor until removed.

3. An electric zinc furnace having therein agglomerated oxid-of-zinc and carbon directly sustained by a porous carbon resistor, electrically heated to transform the charge into volatile forms, and a condenser or condensers constructed and disposed so that at least a part of the evolved fumes and gases pass through the said resistor before entering the said condenser or condensers.

4. In an electric zinc furnace of the character herein described the combination with the carbon resistor of carbon portions contiguous to or forming part of its sides and of carbon-filled condensers whose inlet ends are connected to the said carbon side portions and whose contained carbon connects with the resistor whereby the fumes and gases produced by the reaction are continuously and uninterruptedly maintained in contact with, or contiguous to, a carbon reducing medium.

5. In an electric zinc furnace of the character herein described, the combination therewith of a series of tubular condensers, a chamber built along the outside of said furnace whose outer wall is thinner than the end walls and whose outer walls are thin enough to permit the transfer of heat through the same, and means for heating or cooling the chamber, the condensers being contained within the chamber and whose ends are mounted, respectively in the wall of the furnace and the outside wall of said chamber, as and for the purpose specified.

6. In the metallurgy of zinc the method which consists in successively charging an electric furnace with a mixture of zinc oxid and carbon, continually heating at least a portion of the charge to the temperature at which zinc fumes will be driven off therefrom and oxid of carbon will be formed from the uniting of the carbon and the oxygen of the zinc oxid, withdrawing the zinc fumes as and when formed in the heated-reducing zone, immediately conducting said zinc fumes through hot carbon and condensing said zinc fumes in the presence of hot carbon.

7. In the metallurgy of zinc the method which consists in maintaining on the resistor of the electric furnace a charge comprising zinc oxid and carbon of sufficient depth to prevent the zinc fumes and oxid of carbon from passing therethrough when the process is being carried out, supplying heat, by means of the resistor, to the charge sufficient in amount to reduce the zinc oxid by means of the heat and the carbon to zinc in vaporous form, and to simultaneously therewith form oxid of carbon, and permitting the escape of said vaporous zinc and oxid of carbon from the reducing zone directly in the hot carbon.

8. In the metallurgy of zinc the method which consists in maintaining on the resistor of the electric furnace a charge of zinc oxid and carbon of sufficient depth to prevent the zinc fumes and oxid of carbon from passing therethrough, when the process is being carried out, supplying heat by means of the resistor to the charge to reduce the zinc oxid by means of the carbon to zinc in

vaporous form, and to form oxid of carbon, and permitting the escape of said vaporous zinc and oxid of carbon from the reducing zone; the furnace being successively recharged to maintain the height of the charge and the vaporous zinc and the oxid of carbon being allowed to escape as and when formed directly in the hot carbon, thereby enabling a continuous process to be carried out.

9. An electric furnace having a resistor composed substantially of carbon and carbon lined sides extending above the resistor, the said sides being in loosely agglomerated pieces.

10. An electric furnace having a horizontal carbon resistor, carbon sides extending above the resistor to receive and hold the charge therebetween, condensers leading from the resistor sides to permit the fumes and gases formed at the heating zone of the furnace to pass therethrough.

11. An electric furnace having a resistor composed substantially of carbon, carbon side walls extending above the resistor, and condensers arranged to receive fumes and gases formed in the heat zone of the furnace, said condensers being filled with carbon directly connected with the said carbon sides.

12. An electric furnace having a horizontal resistor, permeable side walls extending above the resistor, condensers arranged to receive the fumes formed in the heated zone adjacent to the resistor and means for effecting or controlling the heating conditions of the condensers; the condensers being filled with carbon directly connected with the said permeable side walls.

This specification signed and witnessed this 12th day of September A. D., 1911.

CHARLES V. THIERRY.

Signed in the presence of—
CLAUDIUS LUSSON,
H. C. COXE.