March 15, 1949. S. ROBSON ET AL 2,464,262

PRODUCTION OF ZINC

Filed May 12, 1944 2 Sheets-Sheet 1

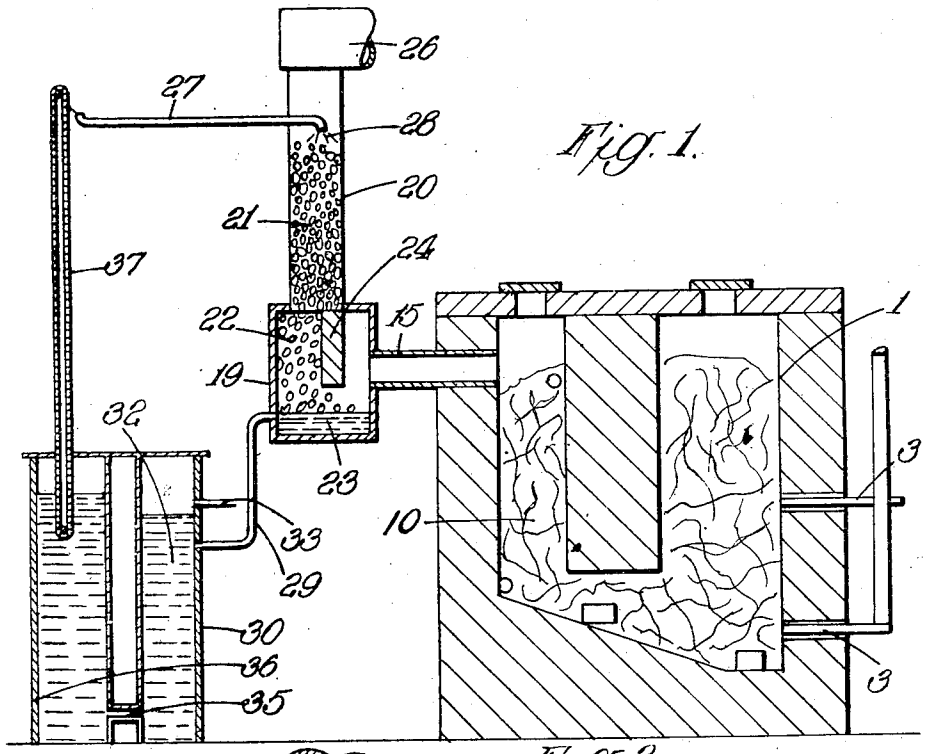


Fig. 1.

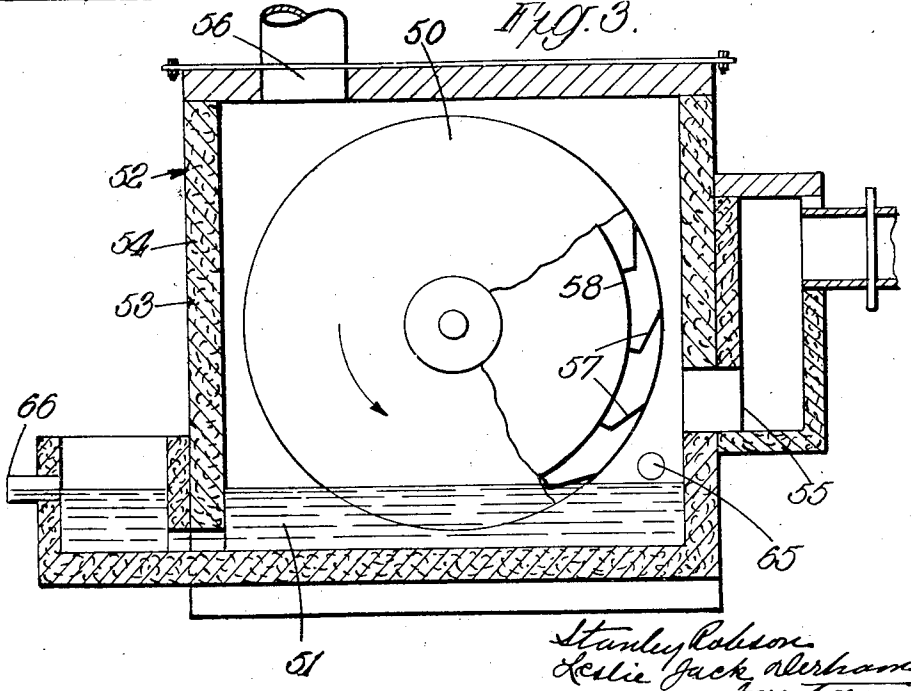


Fig. 3.

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Fig. 2.

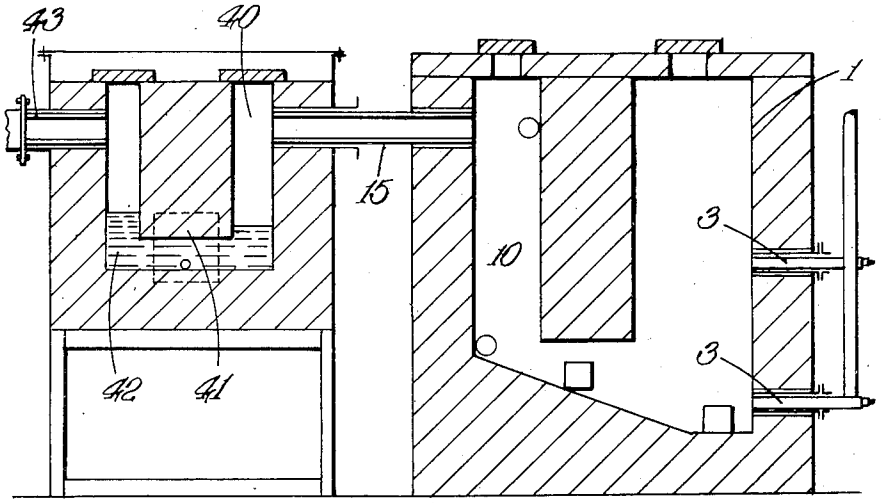
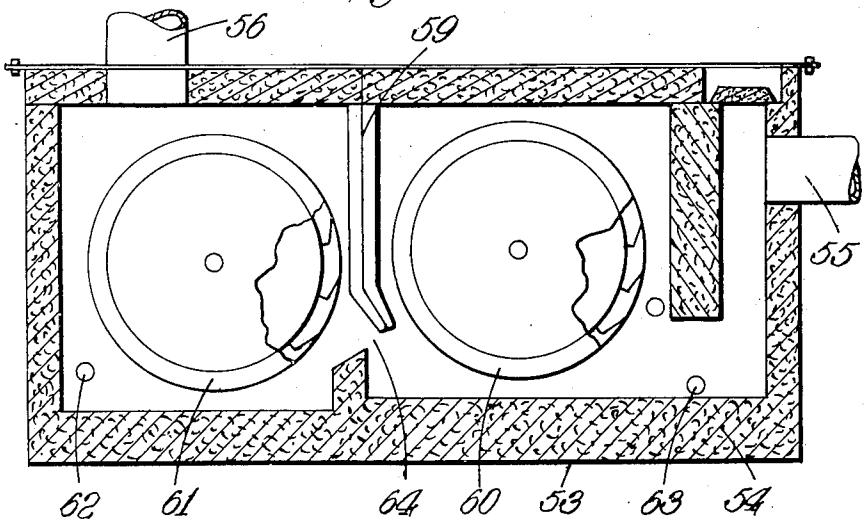


Fig. 4.



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Patented Mar. 15, 1949 2,464,262

UNITED STATES PATENT OFFICE

2,464,262

PRODUCTION OF ZINC

Stanley Robson, Clifton, Bristol, and Leslie Jack Derham, Severn Beach, England, assignors to The National Smelting Company Limited, London, England, a British company

Application May 12, 1944, Serial No. 535,290
In Great Britain March 13, 1943

Section 1, Public Law 690, August 8, 1946.
Patent expires March 13, 1963

1 Claim. (Cl. 75—86)

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In the production of zinc it is often necessary to condense zinc vapour from a gaseous mixture and difficulty is generally encountered in obtaining all the zinc as molten metal and avoiding the formation of zinc dust. Particularly when the concentration of zinc in the gas is low, as is the case when zinc is reduced from a sintered ore in a blast furnace, the difficulty of collecting the zinc as molten metal becomes a major problem and it has been an important factor in the failure of the many attempts so far made to produce zinc by blast furnace operation. A similar difficulty has arisen in the electrothermic smelting of zinc. The principal cause of the difficulty is oxidation by carbon dioxide by the reaction

$$Zn+CO_2=ZnO+CO$$

This reaction, unless the concentration of carbon dioxide is small, can occur above the dew-point. Even if only a fraction of the total zinc is thus oxidised, it is found that the difficulty of condensing the remainder to molten metal is increased. A possible explanation is that when the dew-point is reached any particles of zinc oxide act as nuclei for the condensation of metallic zinc. These droplets of metallic zinc can then be further oxidised on the surface. This superficial oxide film then probably tends to prevent the droplets coalescing, even if they are brought into contact with molten zinc.

An important object of this invention is to provide an improved process for condensing zinc vapour from a gaseous mixture.

Another object of this invention is to make use of the properties of lead or lead-rich alloys in the condensation of zinc.

In our invention zinc vapour is condensed by bringing the gases into intimate contact with molten lead or molten alloy rich in lead that is at a temperature which is not greater than 550° C. We place the condensing apparatus as close as possible to the outlet by which the gases leave the retort or furnace, to ensure that the zinc-bearing gases, while still hot, are brought into contact with the molten lead as soon as possible. Rapid chilling of the gas is thereby effected, and any considerable amount of oxidation of zinc by carbon dioxide or other gases present is avoided.

The lead must be at a relatively low temperature for two reasons. Firstly, it is necessary to shock-chill the zinc, and secondly the gases will necessarily retain an amount of zinc proportional to the vapour pressure of zinc over the solution of zinc in lead that is formed by the condensation, and the lower the temperature the

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lower this proportion will be. If the initial gaseous mixture contains only a small amount of zinc vapour, the fraction of this that cannot be condensed will be high unless the liquid lead is at a low temperature. For these reasons the lead is preferably at a temperature below 500° C. and is generally at a distinctly lower temperature.

Zinc is sparingly soluble in lead, the solubility increasing with the temperature, so the use of molten lead for condensing the zinc presents the great advantage that the zinc dissolved in the lead can be recovered when the lead is cooled. The zinc may be obtained either directly as a liquid or as a solid floating on the surface of the molten lead. After the separation of the condensed zinc the lead may be used again for the condensation of further zinc vapour, that is to say, it may be continuously circulated as a liquid; this can easily be done in view of the low melting point of lead.

The very sparing solubility of zinc in lead, which is advantageous for the reason just given, makes the lead have only a small power to remove zinc by solution from a gaseous mixture at temperatures above the dew-point of the gaseous mixture. In our invention the low temperature at which the lead is maintained serves to reduce the temperature of the zinc to below the dew-point and so the zinc is easily condensed and dissolved.

It is generally found advantageous to maintain a considerable degree of turbulence in the lead. A possible explanation of its effect is that, if any zinc vapour is condensed as dust and becomes superficially oxidised, vigorous agitation of the lead helps to rupture or prevent the formation of a coherent oxide film, so that the metallic particles can dissolve in the liquid lead.

As a rule, ordinary commercial lead is used, but the condensation can be effected equally well by means of a lead-rich alloy provided that the other element or elements of the alloy dissolve in lead in preference to zinc so that they will not contaminate the zinc to any great extent after it has been separated from solution in the lead.

Some plants in which the present invention may be carried out are shown diagrammatically in the annexed drawings, in which—

Figure 1 is a longitudinal vertical section through one plant;

Figure 2 is a similar section through another plant; and

Figures 3 and 4 show two other forms of condenser.

In the plant shown in Figure 1 zinc is pro-

duced from oxides or ores by reduction in a blast furnace comprising a shaft 1 with tuyères 3. As the charge moves down this shaft, a gaseous mixture of zinc vapour, nitrogen, carbon dioxide and carbon monoxide is evolved and passes to a heated coke column 10, in which some reduction of carbon dioxide to carbon monoxide takes place, all as described in detail in the application of Stanley Robson, Stephen E. Woods and Leslie J. Derham, Serial No. 535,288, of even date herewith and now abandoned. The gases leave the coke column through a duct 15 and at this point the composition of the gaseous mixture may, for example, be 5% Zn, 63% N, 5% CO_2 and 27% CO.

The condenser shown in Figure 1 is constituted by a packed tower up which the gases are passed in counter-current with molten lead. The gaseous mixture first enters a chamber 19 which is packed with coke 22 and is surmounted by the tower proper 20, which is packed with somewhat finer coke 21. Liquid lead is introduced above this complete coke column by a pipe 27 that terminates in a spraying nozzle 28, so that a flow of liquid lead is maintained down the coke column. A baffle 24 prevents the lead from flowing laterally into the duct 15. The incoming gases flow upwards through the column in countercurrent with the molten lead, and most of the zinc vapour is condensed out and dissolves in the lead. A substantial part of the heat that must be removed from the gas in order to cool and condense the zinc vapour is taken up by the lead, which may rise in temperature by from 100 to 200° C. during its passage through the condenser. The gases leave the top of the tower by a pipe 26, by which they are conducted to a dust chamber (not shown) to recover the remainder of the zinc as metallic dust. The lead containing, say, 1.5% zinc in solution and at a temperature of about 500° C. forms a pool 23 at the bottom of the chamber 19 and leaves by an outlet pipe 29 to a cooling bath 30. The heat loss from this is so controlled, for example by providing different thicknesses of insulation, that the upper surface 32 of the lead in the bath is at a temperature greater than 418° C., say about 500° C., but the lead at the bottom of the bath is at a lower temperature, say about 340° C. Zinc crystals come out of solution from the lead at the bottom and float to the top where they melt so that a layer of liquid zinc is formed at the top and is withdrawn from time to time through an outlet 33. From the bottom of the bath 30 the lead, containing about 1% of zinc in solution, is carried by a pipe 35 to a reservoir 36, whence it is conveyed by a hoist 37 or other appropriate means to the pipe 27 and thence back to the top of the condensing tower. A convenient rate of circulation of the lead is from 100 to 200 times by weight the amount of zinc removed from the gas.

It will be understood that other packing materials may be used, e. g. refractory materials such as carborundum.

In the form of condenser shown in Figure 2, the gases bubble through the lead beneath a baffle that projects downwards into a bath of the liquid lead. As before, gases from a blast furnace 1 arrive by a duct 15 and they enter a closed chamber 40 containing a baffle wall 41. A pool of molten lead 42 is maintained in the chamber in an amount sufficient to keep the bottom of the wall 41 immersed. Suction is applied to the outlet pipe 43 by a pump (not shown), and in consequence the gases bubble through the

pool of molten lead and in passing under the wall 41 they produce a spray of liquid metal which is particularly effective in scrubbing the gas. Some of the lead is withdrawn continuously and circulated through a cooler such as that shown in Figure 1. The type of condenser shown in Figure 2 is simple, but not as efficient as that shown in Figure 1, probably because bubbles of gas tend to surge rapidly through the lead beneath the wall 41.

The form of condenser shown in Figure 3 is particularly efficient in extracting a large proportion of the zinc vapour from the gases as molten zinc. In principle, the gases are caused to pass through a spray or curtain of molten lead. This is produced by causing a rotary paddle-wheel 50 to dip into a pool of molten lead 51 in a box 52 having an outer steel casing 53 and a brick lining 54. The gases enter at 55 and leave at 56, and in their passage they are forced to pass through a spray of lead that is forced upwards by the vanes 57 of the wheel as the latter is rotated anti-clockwise at a speed of, say, 100 to 120 revolutions per minute. These vanes are enclosed within a perforated plate 58 through which the molten lead can easily pass. Of course, the wheel 50 must extend from one side of the box 52 to the other so as to ensure that the spray extends completely across the box. The lead is fed in at 65 and discharged at 66.

If it should be found that a single spray is insufficient two paddle-wheels 60 and 61 may be used in series as shown in Fig. 4, the gases passing from one to the other through an opening 64 in a partition 59. Some of the lead thrown up by the second paddle-wheel 61 will pass into the compartment in which the first wheel 60 works, so the incoming lead may simply be introduced into the second compartment through an inlet 62 and removed from the first compartment by an outlet 63.

Naturally the paddle-wheels shown may be replaced by any equivalent devices which will produce a stray and promote turbulence.

The invention may usefully be applied to any mixture of zinc vapour and other gases from which difficulty is experienced in obtaining an adequate recovery of molten zinc. It is, however, particularly valuable in the condensation of zinc from gases obtained by smelting zinc ores in a blast furnace as described in the said application of Stanley Robson, Stephen E. Woods and Leslie J. Derham. It is also valuable in the condensation of zinc from the gases from an electrothermic arc furnace in which oxidised zinciferous materials are reduced by carbon. When treating such gases, relatively rich in zinc vapour as compared with those from a blast furnace, it is not so important that the lead should be maintained at below 500° C., but it is still preferable that its temperature should be kept as low as the other operating conditions permit.

When zinc is smelted in externally heated vertical retorts or in vertical electric resistance furnaces, it is found desirable to introduce some gas or air into the bottom of the retort or furnace. The amount of such gas that can be introduced is limited because large quantities would dilute the zinc vapour so that an unduly large amount of zinc dust would be formed in the customary types of condenser. If the gases from such vertical retorts or furnaces are treated by the condensation methods of the present invention, the amount of gas or air introduced at the bottom of the retort or furnace can be increased to the ex-

tent required to give the best operating results from the point of view of the furnace or retort itself, and the zinc evolved can still be efficiently condensed to liquid metal.

What we claim is:

The method of recovering zinc from zinc ore which comprises smelting the ore in a blast furnace with resultant formation of a gaseous mixture containing zinc vapor, carbon monoxide and a substantial amount of carbon dioxide, bringing the gaseous mixture while still hot into intimate shock-chilling contact with circulating molten lead in a condensing zone maintained at a temperature not greater than 550° C. to cause the gaseous mixture to cool to a temperature below that at which the carbon dioxide can react with the zinc to form objectionable zinc oxide and condensing the zinc vapor as a solution of zinc in the lead, accumulating a body of the solution, cooling the lower portion of said body of solution to a temperature below 418° C. but not below the melting point of lead to precipitate zinc therefrom, while maintaining the upper portion of said body of solution above 418° C., permitting the

precipitated zinc to rise into the upper and hotter portion of said body of solution with resultant remelting of the zinc and the formation of a supernatant layer of molten zinc, and removing molten zinc from said supernatant layer and returning the molten lead from which the zinc was precipitated for reuse in the condensing step.

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