Dec. 19, 1939. J. O. BETTERTON ET AL 2,183,535

RECOVERING ZINC

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Fig. 1

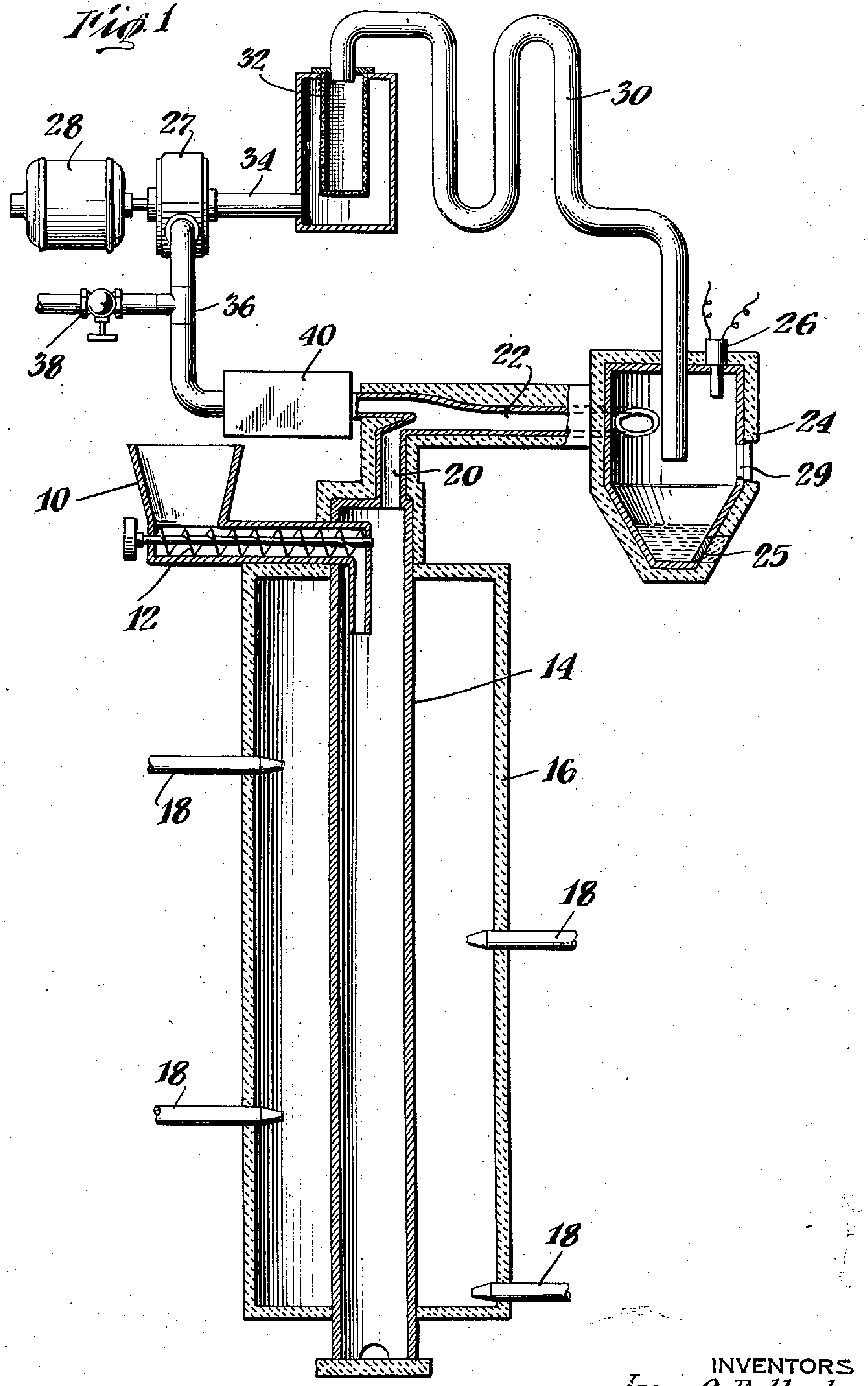

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Fig. 2

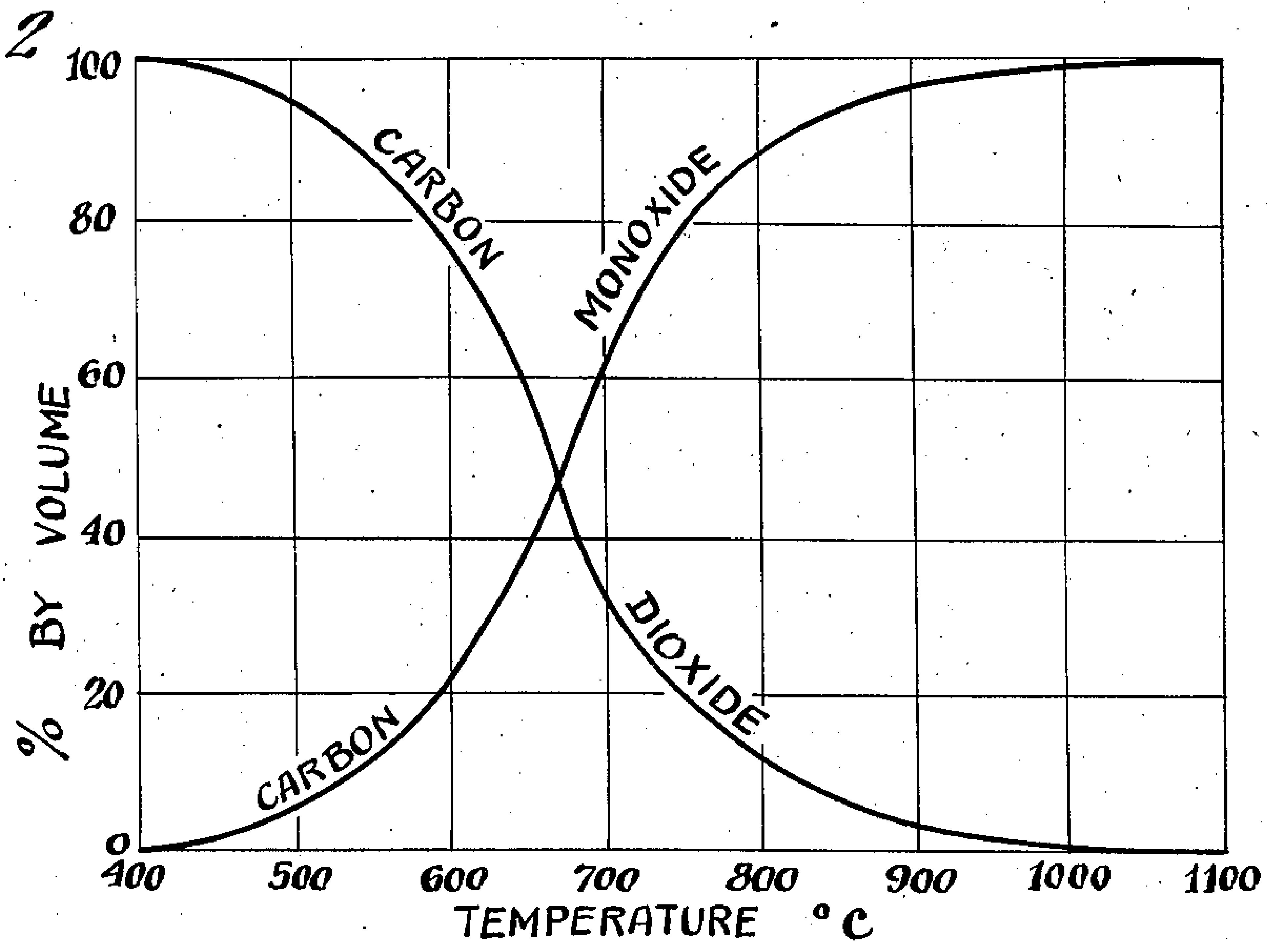
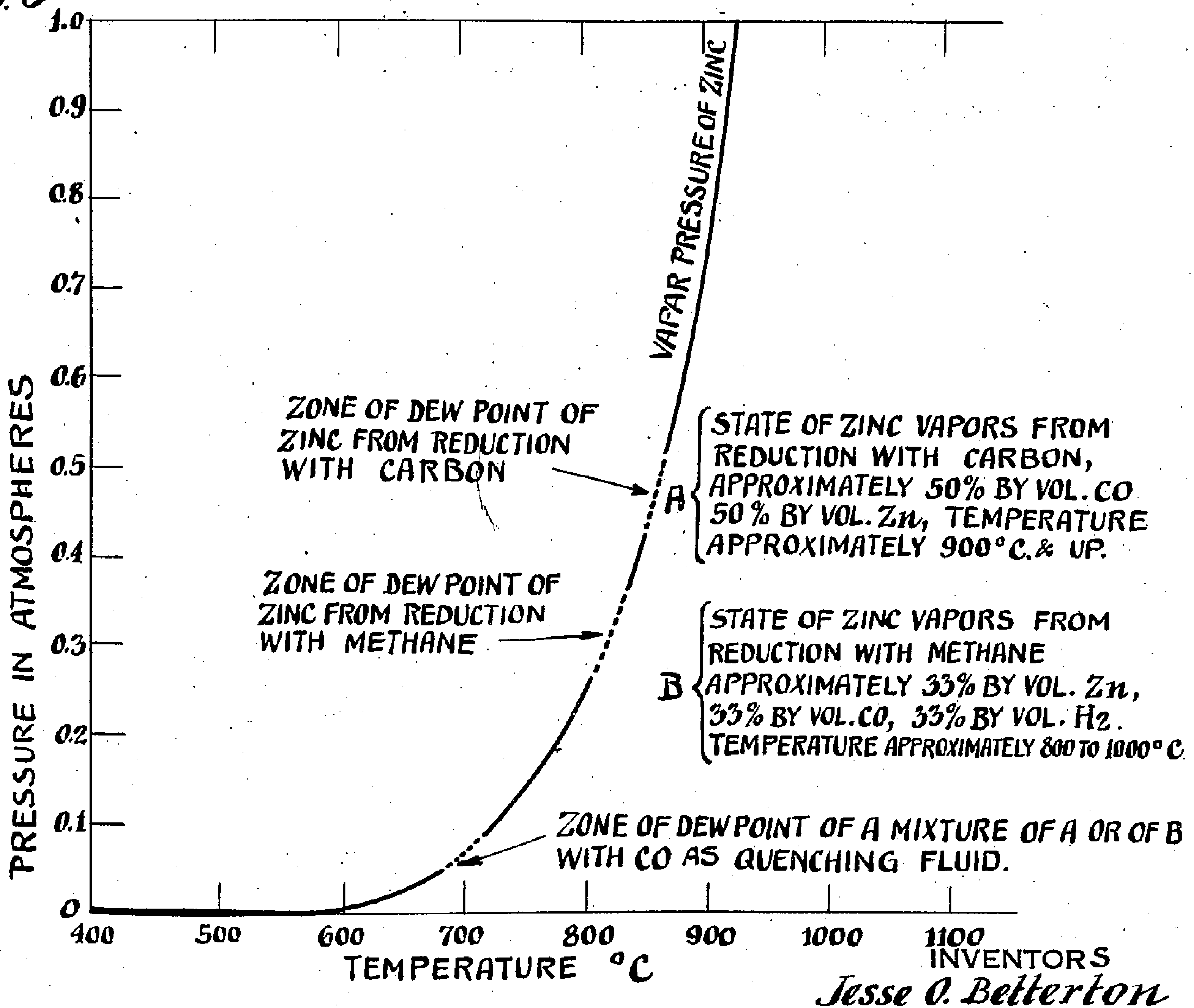


Fig. 3



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2,183,535

## RECOVERING ZINC

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2 Claims. (Cl. 75—26)

This invention relates to the production of zinc.

Various proposals have been advanced in the past for producing zinc by subjecting zinc oxide to a flash reduction and condensing the resulting zinc vapor. In general, these proposals contemplated injecting a finely-divided charge of zinc oxide and carbonaceous reducing agent, with or without flux, into a retort wherein the oxide is reduced in suspension by a suitable reducing gas, e. g., carbon monoxide or methane and immediately thereafter recovering zinc from the gaseous products of reduction by various conventional condensation methods. However, those skilled in the art have been unable to translate such proposals into terms of successful commercial practise.

Subsequently, it was found that the flash reduction of zinc oxide and condensation of the zinc vapor could be successfully practised by conducting the gaseous products of reduction, on their way from the flash chamber to the condenser, through a suitable reducing and filtering medium, e. g., a bed of incandescent coke. For details of such a process the reader is referred to United States Letters Patent No. 2,096,779 granted October 26, 1937 to George P. Bartholomew and Edward P. Fleming to United States Letters Patent No. 2,181,148 granted Nov. 28, 1939 to Melville F. Perkins and Roland G. Crane.

The present invention constitutes a meritorious advance in the art by providing, for the first time. a process in which zinc oxide is flash reduced and the zinc vapor content of the gaseous products of reduction directly condensed and recovered without any intermediate or conditioning treatment. In short, the new process renders it unnecessary to conduct the vapors through a reducing or filtering medium prior to condensation.

In accordance with the invention, zinc oxide is reduced by passing same in a finely-divided, non-compacted state through a suitable reducing atmosphere, directly following which the zinc vapor is subjected to the action of a suitable quenching fluid under such conditions that the temperature of the zinc vapor is lowered to condensation temperature with such speed as to practically eliminate any reoxidation of zinc. The broad process of the invention is, of course, susceptible of many specific applications and accordingly, for purposes of illustration, it will be described, for the most part, with reference to flash reducing the zinc oxide by passing same through a vertical retort with coke dust and the use of carbon monoxide gas as the quenching fluid.

Although the novel features which are believed to be characteristic of this invention will be particularly pointed out in the claims appended thereto, the invention itself, as to its objects and advantages, and the manner in which it may be carried out, may be better understood by reference to the following description taken in connection with the accompanying drawings forming a part thereof in which

Fig. 1 is a diagrammatic, sectional elevation of one form of apparatus for carrying into practise the process of the invention.

Fig. 2 is an equilibrium diagram between carbon monoxide and carbon dioxide showing the percentage of each at given temperatures, and

Fig. 3 is a graphic representation of the vapor pressures of zinc with dew points of various mixtures of zinc with other vapors indicated thereon.

Referring to Fig. 1, there is shown a charge hopper **10** with screw conveyor **12** for delivering charge to flash shaft **14** vertically disposed in furnace **16** which is equipped with burners **18**. Off-take **20** leads from the top of shaft **14** to quenching throat **22**, the latter discharging into collecting or recovery means **24** which is provided with tap **25**, service door **29** and thermocouple **26**. A fan **27** driven by motor **28** is connected on its suction side with collector **24** by pipe **30**, filter **32** and pipe **34**. On the compression side of blower **27** is pipe **36** provided with vent **38**, said pipe passing through temperature control means **40** and into throat **22**.

Employing the apparatus just described, the process of the invention may be practised as follows: the furnace is brought to zinc reduction temperature and a pre-heated, finely-divided charge of zinc oxide and coke fed from hopper **10** to the flash shaft **14** wherein the zinc oxide is reduced as the charge falls to the bottom of the shaft. The reduction may be expressed by the equations

$$ZnO+C\rightarrow Zn+CO$$
$$ZnO+CO\rightarrow Zn+CO_2$$
$$CO_2+C\rightarrow 2CO$$

and is preferably so controlled that the oxide is reduced practically in toto and the gases accompanying the zinc vapor, as it is withdrawn through the off-take **20**, are predominantly carbon monoxide.

As the hot zincky vapors from the off-take **20** enter the throat **22** they are met by and intermixed with a stream of carbon monoxide in which temperature, quantity and velocity are so correlated as to instantly quench the zinc which is recovered in the collector **24**. The zinc is withdrawn as desired through tap **25** and the carbon monoxide is withdrawn through pipe **30**, passed through filter **32** and recirculated to the throat **22** after passing through temperature control means **40**, any excess gas being vented from the system at **38**. Solid particles of fly ash, carbon and the like which may be entrained in the gas stream from the flash reducer can be removed from the collector **24** through door **29**.

The instant and sudden quenching of the hot zinc vapor as contemplated herein minimizes blue powder formation thereby enhancing zinc recovery. This may be better understood by reference to Figs. 2 and 3 and by a consideration of the principles underlying zinc reoxidation and blue powder formation.

It is well known that at certain temperatures carbon monoxide dissociates according to the reversible reaction

$$2CO \rightleftarrows C+CO_2$$

and Fig. 2 shows that at temperatures in the vicinity of 1000° C. the equilibrium condition calls for substantially all carbon monoxide. At such temperature the rate of the producer gas reaction and its reversal is rapid thereby permitting attainment of the equilibrium condition within a short time. At temperatures of, say, 800° C.–900° C., the equilibrium conditions call for appreciable quantities of carbon dioxide but the rate of reaction in the vicinity of these temperatures is very slow thereby requiring long periods of time for attainment of the equilibrium condition. Accordingly, by cooling the gas in a sufficiently short interval of time it is possible to freeze the high temperature equilibrium composition and make it available at lower temperatures.

Now zinc is not reoxidized by carbon monoxide but it is susceptible to reoxidation by carbon dioxide. In this connection the following excerpt from "Zinc Smelting from a Chemical and Thermodynamic Viewpoint" by C. G. Maier, U. S. Department of Commerce, Bureau of Mines Bulletin 324 is pertinent.

"Zinc is a moderately strong basic metal. By analogy with the alkaline earth and alkali metals, which are known to reduce carbon monoxide at elevated temperatures, zinc also might be expected to reduce carbon monoxide. The reaction has been written:

$$Zn(g) \text{ or } Zn(1)+CO=ZnO+C$$

"This equation is obviously the reversal of the steady-state condition of continuous reduction and involves the reversal of the producer-gas reaction

$$2CO=CO_2+C$$

Equation (1) is then not a complete reaction, since carbon dioxide is omitted . . . At 1 atmosphere pressure equilibrium is possible only at 857° C. The mechanism of reaction (1) then consists of the consecutive or simultaneous reactions

$$2CO=CO_2+C$$
$$CO_2+Zn=ZnO+CO$$

Of these the first is known to be slow below about 1,100° C., but the second is perceptible above 300° C. and is very rapid about about 550° C. Then the rate at which zinc is oxidized by carbon is determined by the slow step, the reversal of the producer-gas reaction, or the dissociation of carbon monoxide.

"Reference to the . . . (producer-gas reaction) shows that large amounts of carbon dioxide would be present in the equilibrium mixture at temperatures below 850° C., but it is also known that below 850° C. the rate of dissociation becomes increasingly slow, and in the absence of a very active catalyst months or even years might be necessary to reach the equilibrium concentration."

Referring to Fig. 3, in which typical zinc vapors resulting from the flash reduction of zinc oxide by carbon monoxide and by methane, respectively, are indicated, it will be seen that it is necessary to pass through the zone of rapid reoxidation of zinc (i. e., the zone of rapid reversal of the producer gas reaction) before the dew point of zinc is reached.

By the present process, the quenching fluid cools the zinc vapor from the flash shaft so rapidly that the reversal of the producer gas and other deleterious reactions is, for practical purposes, avoided and the vapor is instantly brought to a temperature, say, below 750° C., at which the rates of such reactions are nil. In fact, not only does the vapor pass through the zone of reoxidation so quickly that the quantity of deleterious products formed by the aforesaid reversible reactions is innocuous but, in addition, it has been found that deleterious components may even be present in appreciable amounts without destroying the commercial value of the process. Once the lower temperature levels have been attained, the danger of appreciable reoxidation is slight and it is simply a matter of completing the cooling and collecting the zinc in a suitable manner.

The term "zinc oxide" in the present specification and claims is used in the generic sense as embracing all ores, calcines, etc., in which zinc is present in the oxidized state.

For purposes of illustration the new process has been described with reference to the use of carbon monoxide in effecting both the flash reduction and the quenching steps but the process is not so limited and may be practised with other mediums within the scope of the appended claims.

What is claimed is:

1. In the art of producing zinc by reducing zinc oxide in gaseous suspension and condensing the zinc vapor, that improvement which consists in directly subjecting the zinc vapor from the reduction operation without intermediate conditioning treatment to instantaneous cooling by intermixing same with a quenching fluid.

2. The process for producing zinc which consists in subjecting a charge comprising zinc oxide and carbonaceous reducing agent to a flash reduction, directly intermixing the gaseous products of reduction containing the zinc vapor with a cold stream of carbon monoxide gas without prior conditioning of the former thereby to immediately quench the zinc vapor to a temperature at which reactions conducive to zinc reoxidation proceed only at harmless rates, and recovering zinc from the quenched vapor.

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