Dec. 30, 1941. H. M. CYR ET AL 2,267,720

APPARATUS FOR MAKING ZINC OXIDE

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Fig. 1.

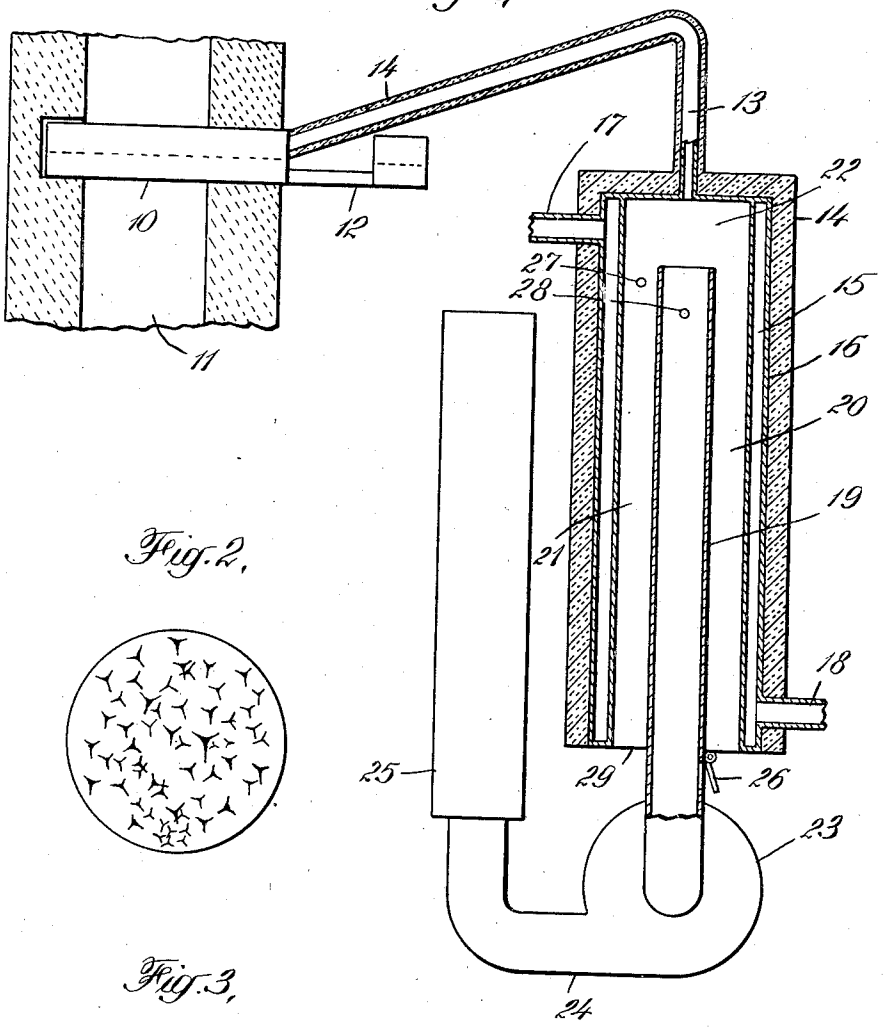
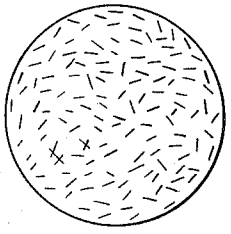


Fig. 2.

Fig. 3.



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APPARATUS FOR MAKING ZINC OXIDE

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11 Claims. (Cl. 23—277)

This invention relates to metallurgical apparatus and particularly to apparatus adapted for the manufacture of zinc oxide. The invention aims to provide an improved apparatus whereby the crystal structure of zinc oxide particles produced by the so-called French process is controlled. More particularly, the invention contemplates the production of acicular zinc oxide by burning zinc vapor derived by boiling zinc metal, as distinguished from the American process in which the zinc vapor is derived directly by reduction of ore. The invention contemplates the production of zinc oxide in which substantially all of the particles are crystals of acicular habit as seen under the microscope and contemplates so controlling the French process of zinc oxide manufacture that substantially all of the particles are well developed single needle-like crystals or else complex crystals such as threelings or fourlings, particles of colloidal dimensions being substantially absent.

There are two types of pyrometallurgical methods of making zinc oxide, the American process and the French process. In the American process, zinc vapor is produced by reducing ore and then burned to zinc oxide while still mixed with products of combustion derived from the reduction fuel. In the French process, zinc vapor is obtained by boiling metallic zinc, and then burned to form zinc oxide. Zinc oxide made by the French process under proper conditions is superior in color and brightness to that made by the American process because zinc vapor obtained by boiling metallic zinc is free from the impurities inherently present in zinc vapor obtained by the reduction of ore.

However, in the American process the crystal habit of the particles of zinc oxide has been more controllable heretofore than in the French process. The French process zinc oxide obtained by known methods and with the use of known apparatus in nodular or cryptocrystalline in crystal habit, and free from acicular crystals; that obtained by the American process can be produced by known methods either in nodular form or in acicular form. Acicular zinc oxide consists of minute needle-shaped crystals, which may be twinned in a complex way to form threelings or the like.

For certain types of paint, acicular zinc oxide is preferred to nodular, since in some conditions and with certain vehicles acicular zinc oxide imparts improved durability to paint; in particular, such acicular zinc oxide decreases the tendency of certain paints to fail by checking and cracking.

The present invention relates to the manufacture of zinc oxide by the French process by burning zinc vapor free from diluting gases and contemplates certain improvements in apparatus by which the crystal habit of the zinc oxide particles is so controlled as to obtain acicular crystals, either individual or in the form of complex twins (threelings or the like). In the zinc oxide produced in accordance with the invention, most or substantially all of the particles are shown by the microscope to be well developed single needle-like crystals or else complex twinned acicular crystals such as threelings or the like; and particles of colloidal dimensions are substantially absent.

Our invention thus permits of the production of acicular oxide having the superior qualities due to high purity, e. g., superior color and brightness.

The apparatus of our invention may be employed for the manufacture of zinc oxide and particularly in a process for making acicular zinc oxide which comprises introducing a stream of substantially undiluted zinc vapor into a combustion zone and burning the zinc vapor in the zone in a current of preheated air. In case the air is preheated only a few hundred degrees C., say to 500° C., the current of air should be slow, and the air should be supplied in only slight excess, say 10%. In case the air is intensely preheated, say to 1000° C. or over, the restrictions mentioned with regard to velocity of the air current and amount of excess air are not necessary. Preferably, the stream of substantially undiluted zinc vapor travels into the combustion zone surrounded by an annular stream of preheated air in which subsequently the zinc is burned, the temperature conditions in the zone being controlled to regulate the crystal character of the resulting zinc oxide. Both temperature control and preheating of the air may be effected advantageously by passing the air to be preheated in countercurrent heat exchange relationship with the burning zinc vapor and hot fume traversing the combustion zone.

Apparatus in accordance with our invention comprises a combustion chamber having a heat conductive refractory wall, an air-preheating chamber comprising an annular portion disposed around said combustion chamber and having an air inlet therein and an end portion communicating with the combustion chamber, means for introducing zinc vapor into said end portion,

e. g., a heat-insulated conduit, a heating chamber surrounding said preheating chamber and combustion chamber, and means for removing zinc oxide from the combustion chamber at a point remote from that at which it communicates with the preheating chamber. In the preferred form of my apparatus, the zinc oxide is withdrawn from the combustion chamber by suction which conveniently may be created by a fan connected to the outlet of the combustion chamber as described hereinafter. A separate preheater for air of any type may also be used.

Acicular zinc oxide, particularly when in the form of threelings and the like, has a tendency to settle and collect on the floor of the combustion chamber in which it is formed, or in the pipe line in the neighborhood of the combustion chamber. This settling of the acicular zinc oxide not only increases the labor required to operate the furnace on account of the frequent cleaning out rendered necessary thereby, but results in the production of much off-grade zinc oxide, since the particles of the zinc oxide that collect in or near the combustion zone grow coarse on account of prolonged exposure to the high temperatures prevailing at these points. In order to obviate the thus caused spoilage of part of the zinc oxide, it is advantageous to place the combustion chamber in a vertical position, with the outlet for zinc oxide fume at the bottom. The combustion chamber is thus actually without any bottom in which zinc oxide could collect. Moreover, it is advantageous to lead off the zinc oxide fume from the combustion chamber into a descending pipe, so arranged that no zinc oxide can collect in a hot zone.

The temperature predominating in the combustion chamber affects the form of acicular zinc oxide produced. For example, in the method and apparatus of the present invention if the predominant temperature in the combustion zone is less than about 1225° C., the particles are well developed threelings or fourlings, i. e., complex twinned acicular crystals. If the predominant temperature is above about 1250° C., the particles are well-developed single needle-shaped crystals. If in practical operations threelings and the like form to an extent that is not desired, such formation may be prevented, and zinc oxide consisting of individual needle-shaped crystals obtained, by raising the temperature of the combustion zone, for example, by more intensive heating of the heating chamber surrounding the preheating chamber and combustion chamber in a preferred form of apparatus in accordance with the invention.

These and other features of our invention will be understood more thoroughly in the light of the following detailed description taken in conjunction with the accompanying drawing in which—

Fig. 1 is a schematic vertical elevation, partly in section, of an apparatus of our invention;

Fig. 2 is a magnified view of zinc oxide produced in accordance with our invention in which substantially all of the particles are threelings or fourlings; and

Fig. 3 is a magnified view of the preferred form of zinc oxide made in accordance with our invention, with substantially all of the particles in the form of well-developed single acicular crystals or needles.

Referring now to Fig. 1, the apparatus has means for vaporizing metallic zinc such as a retort 10, disposed in a horizontal position in a heating chamber 11 and provided with a charging well 12 and an outlet duct 13 for zinc vapor, which should be covered with heat insulating material 14 or heated or otherwise protected from loss of heat to prevent condensation of zinc therein.

The duct connects the retort to a burner assembly, preferably in the form of an upright cylinder 16 with an outer annular heating jacket 15 outside of which is disposed heat insulating lagging 14. The jacket preferably is heated by gas introduced through an upper inlet conduit 17 and withdrawn through a lower outlet conduit 18. Within the jacket is a cylindrical space into which projects concentrically an upright tube 19 of heat conductive material that forms the combustion chamber. The tube projects to within a short distance of the top of the cylindrical space and is open at its upper end. The space surrounding the tube is an air preheating chamber 20 having a lower annular portion 21 open at its lower end to the atmosphere through the annular air inlet 29 and an upper portion 22 with which the combustion chamber (tube 19) communicates at its upper end. A pyrometer 27 is provided near the discharge end of the air preheating chamber; and a pyrometer 28 is provided in the combustion chamber 19 near its upper end.

The tube 19 projects out of the bottom of the burner assembly to a fan 23, the outlet of which is connected by a pipe 24 to a zinc oxide collector such as a bag 25. A valved inlet 26 for false air is provided to supply cooling air for cooling the zinc oxide fume rapidly after it has left the hot zone of the combustion chamber.

In place of the retort shown in Fig. 1, any suitable means for boiling zinc may be employed. For example, the vertical boiler described in United States Patent No. 1,994,355 to Peirce and Waring may be used with advantage.

The burner assembly is built of refractory material capable of resisting the high temperatures within the apparatus. The combustion tube is advantageously made of material of high heat conductivity such as silicon carbide to facilitate the transfer of heat from the combustion zone within the tube to the air entering the assembly through the preheating chamber.

If the heat interchange through the tube wall is sufficiently effective, it may be possible to substitute heat insulation for the heating jacket which surrounds the preheating chamber. However, especially when it is desirable to produce zinc oxide having substantially all of its particles as single needles, it is advantageous to provide a heating jacket for supplying more heat to the incoming air than can be obtained by heat transfer from the combustion zone. Instead of the jacket for hot gases any other suitable heating means may be provided, for example, an electric heating coil wound around the preheater.

The tube need not be set in a vertical position, but such position is preferred, not only from the standpoint of simple construction but because, as hereinbefore indicated, the vertical position of the tube tends to prevent settling of zinc oxide particles within the combustion chamber where continued heating may bring about excessive crystal growth.

In the operation of the apparatus of Fig. 1, zinc vapor in substantially undiluted condition is driven off from a molten bath of zinc in the retort and passes through the duct to the upper portion of the preheating chamber. Conveniently, the bath of molten zinc may be replen-

ished from time to time through the charging well.

Air to be preheated is drawn through the annular portion of the preheating chamber in countercurrent heat exchange relationship with the heat transmitted through the tube wall and in the upper portion of the preheating chamber surrounds the entering concentrated zinc vapor so that the stream of zinc vapor is ignited and enters the combustion chamber enveloped by a peripheral or annular blanket or envelope of preheated air in slight excess of that theoretically required to burn the zinc vapor to zinc oxide. Combustion of the zinc vapor is completed in the combustion chamber, and the heat of combustion, at least in part, is withdrawn through the tube wall to preheat the entering air.

The zinc vapor fume is drawn out of the combustion zone in the tube and subjected to rapid cooling by admixture with false air before it passes through the lower portion of the tube, the fan and the pipe to the bag or other collecting means. The resulting acicular zinc oxide particles are retained in the bag and the residual gases are wasted therethrough.

Fig. 2 shows the crystal form, magnified several hundred diameters, of zinc oxide made in the apparatus of Fig. 1 with a predominant temperature of about 1200° C. in the combustion zone. It will be observed that substantially all of the particles are well developed threelings and fourlings of substantially uniform size. By raising the predominant temperature in the combustion zone to 1300° C., the formation of complex twinned crystals was prevented, and simple needles, such as those illustrated in Fig. 3, were formed.

We claim:

1. Apparatus for the manufacture of zinc oxide which comprises a first chamber, a second chamber disposed within the first chamber and opening thereinto near an end portion thereof, said second chamber having a wall of refractory material, means for introducing zinc vapor into said end portion, means for introducing an oxidizing gas into the other end portion of the first chamber, means for heating the gas thus introduced, and suction-producing means for withdrawing zinc oxide from the second chamber at a point remote from that at which it opens into the first chamber.

2. Apparatus for zinc oxide manufacture which comprises a combustion chamber having an open end, a preheating chamber having an annular portion disposed around said combustion chamber and separated therefrom by a heat-conductive wall of refractory material and an end portion surrounding the open end of the combustion chamber, means for introducing zinc vapor into said end portion, means for introducing air into said annular portion, an outlet for zinc oxide from the combustion chamber at a point remote from said open end and means for creating a suction in said outlet to withdraw the zinc oxide therefrom.

3. Apparatus for zinc oxide manufacture which comprises a combustion chamber of refractory heat-conductive material, an air preheating chamber comprising an annular portion disposed around the combustion chamber and an end portion communicating with said combustion chamber, means for introducing zinc vapor into said end portion, an inlet for air into said annular portion, means for heating the gas in the annular portion of the preheating chamber, a heating jacket disposed around said annular portion, a layer of insulation disposed around the heating jacket and means for removing zinc oxide from the combustion chamber at a point remote from that at which the combustion chamber opens into the preheating chamber.

4. Apparatus for zinc oxide manufacture which comprises an elongated upright combustion chamber enclosed by a wall of refractory material, an air preheating chamber comprising an annular portion disposed around the combustion chamber and an upper end portion communicating with the combustion chamber, means for introducing zinc vapor into said end portion, an inlet for air into said annular portion, means for drawing the zinc vapor and the preheated air into the combustion chamber and means for sucking zinc oxide fume from the bottom of the combustion chamber.

5. Apparatus for zinc oxide manufacture which comprises a combustion chamber walled with heat-conductive refractory material, an air preheating chamber comprising an annular portion disposed around the combustion chamber and an end portion into which the combustion chamber opens, means for introducing zinc vapor into the end portion, an inlet for air into the annular portion, a heating jacket disposed around the annular portion, and means for removing zinc oxide fume from the combustion chamber at a point remote from that at which it opens into the preheating chamber and adjacent to the air inlet into the annular portion of the preheating chamber.

6. Apparatus for zinc oxide manufacture which comprises a combustion chamber having a heat-conductive refractory wall, an air preheating chamber comprising an annular portion disposed around the combustion chamber adjacent the wall and an end portion into which the combustion chamber opens, a layer of insulation disposed around the air preheating chamber, means for introducing zinc vapor into the end portion, an inlet for air into the annular portion, means for drawing air and the zinc vapor into the combustion chamber, suction-producing means for removing zinc oxide fume from the combustion chamber at a point remote from that at which it opens into the preheating chamber and heat insulating means disposed around the preheating chamber.

7. Apparatus for the manufacture of zinc oxide which comprises an elongated combustion chamber having a heat conductive refractory wall, means for introducing zinc vapor into a central end portion thereof, means for preheating air, means for introducing the preheated air around the periphery of the chamber adjacent the point of introduction of the zinc vapor, means for withdrawing by suction zinc oxide fume from the other end portion of the chamber, and means for removing progressively increasing quantities of heat through the wall of the chamber toward the end portion thereof from which the zinc oxide fume is withdrawn.

8. Apparatus for the manufacture of zinc oxide which comprises an elongated combustion chamber walled with heat-conductive refractory material, means for introducing zinc vapor centrally into an end portion thereof, means for introducing air into the chamber around the stream of zinc vapor, means for passing the air prior to its introduction into the chamber in countercurrent heat exchange relationship with products of

combustion of the zinc vapor in the combustion chamber and means for sucking from the combustion chamber zinc oxide fume formed therein from a point remote from that at which the zinc vapor is introduced.

9. Apparatus for the manufacture of zinc oxide which comprises a combustion tube with a heat conductive refractory wall, means for introducing zinc vapor into a central end portion of the tube, means for introducing preheated air into a peripheral end portion of the tube around the zinc vapor and in contact therewith, suction-producing means for withdrawing products of combustion of the zinc vapor and the air from the other end of the tube, and means for passing a current of relatively cold fluid along the outside of the tube in countercurrent heat exchange relationship with said products of combustion within the tube.

10. Apparatus for the manufacture of zinc oxide which comprises a combustion chamber having a conductive refractory wall, means for introducing zinc vapor into a central portion of said chamber at an end thereof, means for preheating air, means for introducing the preheated air into a peripheral portion of said chamber at said end, means for withdrawing the products of combustion of the zinc vapor and the air from the opposite end of said chamber by suction, and means for passing a cooling fluid along the outside of said chamber in a direction opposite to that in which the products of combustion are passed through the chamber.

11. Apparatus for the manufacture of zinc oxide which comprises an upright elongated tube with a heat conductive refractory wall and open at its upper end, a chamber disposed around the tube and open at its lower end, a conduit for introducing zinc vapor into the chamber above the upper end of the tube, and means for creating a suction at the lower end of the tube to withdraw zinc oxide fume therefrom.

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