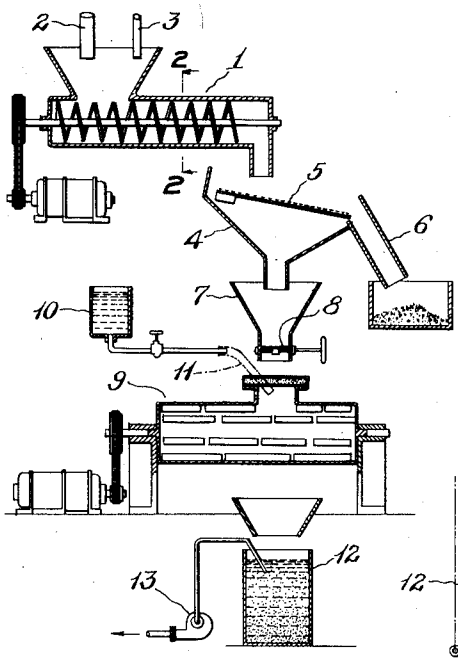
Nov. 22, 1949 J. L. YOUNG 2,489,116

METHOD OF TREATING METALLIC POWDERS

Filed May 3, 1946



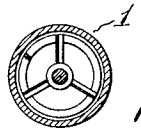


FIG. 2.

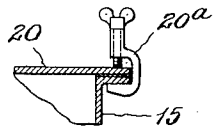
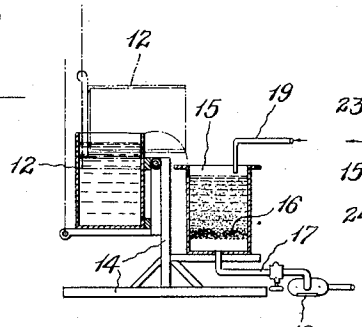


FIG. 3.



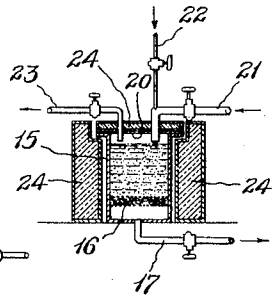


FIG. 1.

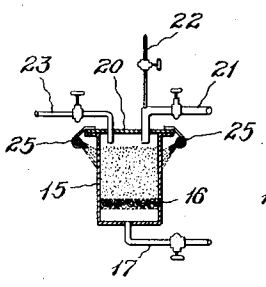


FIG. 4.

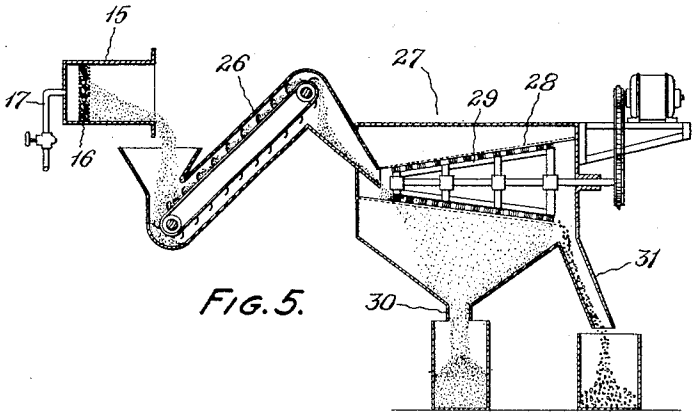


FIG. 5.

INVENTOR:
JOHN L. YOUNG
BY Ray S. Gehr
ATTORNEY.

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METHOD OF TREATING METALLIC POWDERS

John L. Young, Pittsburgh, Pa., assignor to The S. K. Wellman Company, Cleveland, Ohio, a corporation of Ohio

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7 Claims. (Cl. 148—13.2)

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The invention relates to a method of treating metallic copper powders.

In the preparation and treatment of metallic powders drying of the powder becomes necessary in various cases and for various reasons. Under prior practice the drying has been an expensive operation, particularly in the case of metals such as copper that are easily oxidizable and that should be free of oxide for satisfactory use. An important example of such uses is found in powder metallurgy where, in many instances, metallic powder or powder mixtures containing metallic powder predominantly, are compressed in molds or dies to form compacts which are heated to effect sintering and, oftentimes, simultaneous welding to a metal support or carrier. United States patents to Wellman No. 2,178,527 and Swartz Reissue No. 22,282 disclose examples of such treatments and such sintered and welded products.

The fabrication and sintering of such compacts involve problems such as the expansion of the green or unsintered compact as it is ejected from the forming die with consequent tendency to fracture of the compact, the insufficient strength of the green compact to permit the necessary handling prior to sintering and the tendency to undue weakness of even the sintered body if the metallic particles of the powder used are not sufficiently free of oxide film.

Copper powder is very extensively used in powder metallurgy and other fields of use and it is an object of the invention to provide a method of treating copper powders, including the drying thereof, which can be carried out without oxidation of the metal, with simple apparatus and at relatively low cost in labor and materials.

A further object of the invention is to provide a method such as last referred to in which the metal is effectively annealed during the drying without substantial increase in the cost of the treatment.

Another object of the invention is to provide a method of treating copper powders capable of removing oxide film from the metallic particles and thereafter simultaneously drying and annealing the deoxidized material without reoxidation.

It is also an object of the invention to provide a method for the production of an improved copper powder characterized by freedom of the metallic particles from oxide film and moisture, by an annealed state, and by small size and irregular or dendritic form of the metallic particles..

With the above stated objects in view the improved method comprises steps as follows. If the metallic powder to be treated has in some way acquired a coating of oxide film, the powder is first given a deoxidizing treatment in which it is subjected to the action of acid and washing with water. Following this the mass of wet metallic powder is subjected in an enclosed space to the action of a current of superheated steam, with exclusion of air from contact with the mass, until the mass is substantially free of moisture. Then the steam in the enclosed space while still in the superheated state is replaced with an atmosphere that is non-oxidizing to the metallic powder at all temperatures from that of the superheated steam down to normal room temperature. And finally the powder is cooled while exposed to the non-oxidizing atmosphere. The drying of the powder will ordinarily be carried out at a superheated steam temperature and for a time that will effectively anneal as well as dry the metal. If the powder to be treated is free of oxide film the acid treatment may, of course, be omitted.

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By the improved treating method copper powder can be produced that is peculiarly suited for powder metallurgy uses, and at a cost that is notably lower than is possible by other methods. This will be more fully apparent from the detailed description which follows.

As illustrative of all phases of the improved method and products the application of the method to the treatment of copper precipitate will now be described in connection with the accompanying drawing which shows diagrammatically apparatus suitable for the treatment.

In the drawings,

Fig. 1 shows partly in elevation and partly in section various pieces of apparatus designed to effect acid treatment, washing and drying of the metallic powder.

Fig. 2 is an enlarged section taken on the line 2—2 of Fig. 1.

Fig. 3 is a fragmentary section indicating the type of clamp device that can be employed in connection with an autoclave shown in Fig. 1.

Fig. 4 shows cooling devices for use in connection with the autoclave to cool the dried material.

Fig. 5 illustrates screening apparatus suitable for use in breaking up the slightly caked material which results from the drying operation and in classifying the powder particles according to size.

In the commercial production of copper precipitate, sometimes called cement copper, the procedure is often relatively crude and various impurities and foreign matters are mixed with

the metal. This will be apparent from a typical procedure in which suitable copper-bearing raw material, such, for example, as oxidic copper ores, roasted or oxidized copper sulphide ores, and impure scrap metal, are leached to form a copper compound in solution, the solution is separated from undissolved solids of the raw material, and then contacted with scrap iron, tin plate, zinc, aluminum or the like capable of reacting with the copper compound in solution to precipitate metallic copper in comminuted form. As is well known, copper precipitated from solution, with or without application of an externally generated electric current, is dendritic in form and, as a result, even very fine particles of such copper are irregular in form. Commonly the comminuted cement copper has mingled with it copper oxides, iron oxide, calcium oxide, silica and particles of the precipitating metal or metals. Also, by reason of the highly oxidizing conditions under which the cement copper is produced the copper particles are likely to be heavily coated with films of copper oxide.

In the application of the present method to the wet copper precipitate of the character described the liquid mixture may be introduced into the motor-driven mixer 1, as through conduit 2, and simultaneously combined with water introduced through pipe 3 to bring the mass to a suitable consistency for the acid treatment. The mixer, of the spiral agitator type shown in Figs. 1 and 2, mixes and advances the liquid with suspended solids to the discharge end of the mixer where it is delivered to a hopper 4 fitted with a vibration type screen 5 which catches the solid material and discharges it through conduit 6, while the liquid with fine suspended solids passes the screen and is discharged by the hopper 4 into a second hopper 7 fitted with a hand valve 8 which serves to stop flow through hopper 7 when desired.

From the hopper 7 the suspended precipitate is discharged into a rotatably mounted motor-driven drum 9 for treatment with dilute sulphuric acid. Commercial C. P. 66° Baumé acid is suitable for this purpose and is introduced into the treating drum 9 from a holding tank 10 which for convenience is fitted with a section of flexible hose to discharge into the drum.

During intermittent introduction of the acid the pH of the solution should be checked from time to time to determine the progress of the deoxidizing action of the acid. As long as oxide is present the pH will ordinarily not go beyond 3.5. The acidification should be continued until a pH of 2 is reached. Ordinarily, from 1 to 1.5 pounds of the acid per 100 pounds of the precipitate liquid will be required. Obviously this will vary with variation in the relative amount of metal in suspension and with the degree to which it is oxidized. As is indicated the inner surface of the drum 9 is fitted with lifting flights so that the solution is effectively mixed by the rotation of the drum. A suitable mixing for 15 or 20 minutes has the incidental effect of substantially increasing the fineness of the powder.

When the acid treatment is completed the drum contents are in the form of a sludge and should be promptly discharged into a settling tank 12 from which the clear top liquid can be decanted or siphoned off by means of suction pump 13. The decanted liquid will carry copper sulphate in solution and may be accumulated for periodical precipitation treatment to recover the copper. The decanted liquid may, of course, be filtered to recover suspended solids.

After settling of the solution remaining in tank 12 the latter is transferred to a stand 14 by means of which it can be tipped, as shown by dotted lines, to discharge into the body of an autoclave 15 which also may be supported on the stand 14. The autoclave 15 is fitted, a little above its bottom, with a filter 16 which may suitably be constructed of glass cloth. A grade CSS–93 fiber glass cloth made by Owen-Corning Fiber Glass Corporation has been found satisfactory. This product as ordinarily supplied is coated or treated with organic material which, for the present purpose, should be removed by heating and replaced by a protective coating of material such as silicone resin No. 2052 made by Dow Corning Corporation. The filter cloth so prepared is suitably supported in the autoclave to prevent passage of the finely divided material treated and carry its considerable weight. The bottom of the autoclave is arranged to discharge into a valved conduit 17 fitted with a vacuum pump 18, the autoclave thus fitted being adapted to function as a Buchner funnel in which the deoxidized copper precipitate is washed with water introduced through pipe 19 and drawn off from the bottom of the autoclave through the vacuum pump 18. This washing should be continued until the solution is substantially free of salts and acid. The salts should be washed out with cold water and if iron salts are present the water should be aciduated with weak sulphuric acid. When the salts have been removed the residue of acid can be washed out (to a pH of 6) with hot water, a temperature of about 140° F. being suitable. Three or four hours may be required for the washing by percolation through the mass of powder. When the test for pH shows the solution about free of acid the water supply is stopped and the water discharge conduit 17 closed.

Throughout the above described treatment in the container 12 and the autoclave 15 the wet powder is at all times preferably kept covered with water to prevent access of the atmosphere to the powder. If iron salts are present the water should be kept acid until the salts are removed.

Upon completion of the washing of the copper powder the body of the autoclave 15 is moved from the stand 14 and its cover 20 applied and made tight with suitable clamps 20*a* (Fig. 3). Cover 20 is fitted with a valved steam supply pipe 21 which can be connected to a suitable source of superheated steam. Pipe 21 has a valved branch supply pipe 22 adapted to be connected with a source of non-oxidizing gas such as natural gas. Cover 20 is also fitted with a valved discharge or exhaust pipe 23. Sectional heat insulating walls 24, 24 are provided to surround the autoclave during the drying of the copper powder.

To start the drying operation in the autoclave the valve of exhaust pipe 23 is opened and superheated steam is admitted by opening the valve of supply pipe 21. When air in the top of the autoclave has been displaced through the exhaust pipe 23 the latter is closed and the valve of the bottom discharge pipe 17 is opened to start the flow of superheated steam downward throughout the cross-sectional area of the mass of wet powder. At the outset the downward pressure of the steam in the mass will cause discharge of some of the moisture in the liquid state through pipe 17. Thereafter, moisture in the powder is vaporized and absorbed by the superheated steam to be

carried with the latter from the autoclave. By passing the steam downward through the wet powder mass, both gravity and the downward pressure of the gaseous steam unite to prevent channelling of the mass and insure uniform distribution of the steam throughout the mass. The pressure and temperature of the superheated steam may vary widely but, considering the substantial size of the autoclave and the need to maintain a substantial margin of superheat in it, moderate pressures, say under 15 pounds per square inch gauge pressure, and fairly high temperatures are desirable. A steam pressure of 8 or 9 pounds per square inch in the top of the autoclave and a temperature (taken in well in the autoclave cover) of about 1000° F. have been found satisfactory in practice. The steam treatment should continue until the powder is fully free of moisture which will occur, with 1000° steam, when the temperature in the bottom of the autoclave reaches about 550 to 575° F. The values of steam pressure and temperature given clearly are not critical but obviously the degree of superheat of the steam in the bottom of the autoclave must be sufficient at the end of the treatment to insure full vaporization of the moisture present, in order to attain complete drying of the powder.

Such a treatment by superheated steam carried out at temperatures such as specified for a period of about six hours necessary to effect complete drying will, by reason of the prolonged treatment, simultaneously effectively anneal the copper powder.

On completion of the steam treatment of the powder the steam inlet valve in pipe **21** is closed and the valve in inlet pipe **22** is opened to admit a non-oxidizing gas, such as natural gas, which serves to displace the superheated steam in the autoclave. When this has been accomplished the sectional insulation **24, 24** of the autoclave is removed and water sprays **25, 25** (Fig. 4) mounted on the autoclave to cool it and its contents to room temperature. This cooling may require from two to three hours.

During the steam treatment in the autoclave the powder tends to cake slightly but without sintering to any material extent. It is believed that this effect is due to salts of iron and aluminum present in the acid copper precipitate mass which during the washing in the autoclave are hydrolyzed and form thin films of iron and/or aluminum hydroxide on the copper particles. Such coating films, while causing the slight caking referred to, have the beneficial effect of preventing any substantial sintering during the prolonged heat treatment in the autoclave.

To restore the mass of slightly caked material to completely powdered form the charge of the autoclave is dumped into the hopper of a conveyor **26** (Fig. 5) which discharges to a screening apparatus **27** comprising a conical screen **28** with rotary brush **29** which serves to brush the fine material through the screen for discharge through opening **30** and allow any coarse particles to discharge separately through spout **31**. An 80-mesh screen is suitable for the purpose. The metal powder discharged from the screening apparatus **27** should be promptly sealed in air-tight containers to avoid absorption of moisture and resultant oxidation. Those steps of the process including the opening of the cooled autoclave and the final screening of the powder may to good advantage be carried out in an air-conditioned room in which the relative humidity is kept at a low point.

It will, of course, be understood that such portions of the treating apparatus as are used in the wet part of the treatment (including the steam-circulating conduits associated with the autoclave) should be made of material suitably resistant to corrosion. Nickel-chromium alloy has been found satisfactory for the purpose.

Typical commercial copper precipitates, neglecting moisture, run about 90% copper the major part of which is very finely divided. Such material subjected to the method of treatment which has been described produces a product which is 99% or more copper of which about 95% will pass a 300-mesh screen. Furthermore, this material is thoroughly dry, free of oxide film, very soft from the annealing effect of the steam treatment and has the irregular or dendritic particle form characteristic of precipitated copper.

Such a product is admirably suited for powder metallurgy uses previously referred to. Because of the small particle size, freedom from oxide film, irregular form and softness of the powder it forms compacts for sintering of relatively great strength in the green state so that breakage of the unsintered compacts during necessary handling prior to sintering is minimized. Those familiar with this class of work will readily understand that this is due to the fact that the three properties referred to favor the firm locking together of the powder particles when the powder is compressed to form a compact. Furthermore, it is found that compacts made of copper powder treated by the improved method have an expansion on removal from the constraint of the forming die which is substantially lower than that characteristic of other powders. The combined result is a markedly lower loss from breakage of unsintered compacts than is attainable with other copper powders. Also, these notable advantages are secured at a considerable saving in production cost of the copper powder because of the nature of the raw materials which can be used and the low cost both in labor and materials involved in carrying out the improved method of purification and drying. For example, the quality, for powder metallurgy uses, of the product produced from copper precipitate by the improved method is superior to that of high grade electrolytic copper powder which has a much higher production cost because it is produced from higher cost raw material (refined copper), because the electrolytic deposition process is more expensive than the crude precipitation process and because the methods of drying heretofore available are more costly than that of the present method.

In comparison with metal powders produced by mechanical disintegration, the present product is markedly superior for powder metallurgy purposes. The former powders, probably because of their cold working, produce compacts which in the green state are very much weaker than those produced by the present improved product. Indeed the difference in this respect is crucial.

It will be apparent that the present method is applicable to the treatment of copper powders produced in various ways. For example, the electrolytic powders which must be dried from the wet state can be treated in accordance with the present method at markedly lower cost than by prior methods. Again, powders of metal easily oxidized, regardless of the manner in which they are produced, may become badly oxidized before they can be used. Such oxidation greatly reduces

the value of the powder, for at least some uses, but by the use of the present method of treatment such oxidized powder can be fully restored to a high quality condition both with respect to freedom from oxide and softness.

What is claimed is:

1. The method of treating copper powders which comprises the steps of treating the powder with sulphuric acid solution to remove oxide coating from the powder particles; washing the acid-treated powder with water to substantially free it from acid solution; subjecting the substantially oxide-free mass of wet powder in an enclosed space to the passage substantially uniformly through the mass of superheated steam until the mass of powder is substantially free of moisture and meanwhile excluding air from contact with the powder; replacing the steam in the enclosed space while still superheated with an atmosphere that is non-oxidizing at all temperatures from that of the superheated steam down to normal room temperature; and cooling the powder while it is exposed to the non-oxidizing atmosphere.

2. The method of treating copper powders as claimed in claim 1 in which the powder is maintained substantially free from contact with air during the washing thereof.

3. The method of treating copper powders as claimed in claim 1 in which the superheated steam is passed downward through the mass of powder.

4. The method of treating copper powders as claimed in claim 1 in which the superheated steam is passed through the powder at a temperature and for a time sufficient to anneal the metal particles.

5. In a method of treating moisture-containing copper powders, the steps of subjecting the mass of wet powder in an enclosed space to the passage substantially uniformly through the mass of superheated steam until the mass of powder is substantially free of moisture and meanwhile excluding air from contact with the powder; replacing the steam in the enclosed space while still superheated with an atmosphere that is non-oxidizing at all temperatures from that of the superheated steam down to normal room temperature; and cooling the powder while it is exposed to the non-oxidizing atmosphere.

6. The method as claimed in claim 5 in which the superheated steam is passed in a downward direction through the mass of powder in the enclosed space.

7. In a method of treating moisture-containing copper powders, the steps of subjecting the mass of wet powder in an enclosed space to the passage substantially uniformly through the mass of superheated steam at a temperature and for a time sufficient both to free the powder of all moisture and to anneal its metal particles and meanwhile excluding air from contact with the powder; replacing the steam in the enclosed space while still superheated with an atmosphere that is non-oxidizing at all temperatures from that of the superheated steam down to normal room temperature; and cooling the powder while it is exposed to the non-oxidizing atmosphere.

JOHN L. YOUNG.

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