Patented Oct. 8, 1940 2,216,770

UNITED STATES PATENT OFFICE

2,216,770

METHOD OF MAKING METAL POWDERS AND PRODUCT

Joseph E. Drapeau, Jr., Calumet City, Ill., and Louis G. Klinker, New Castle, Pa., assignors to The Glidden Company, Cleveland, Ohio, a corporation of Ohio

No Drawing. Original application February 11, 1937, Serial No. 125,303. Divided and this application April 10, 1939, Serial No. 267,186

11 Claims. (Cl. 75—0.5)

This invention relates to the production of metallic powders and has particular reference to a new and novel method of producing these powders involving pyro-metallurgical processes.

Metal powder in the form of flakes carrying a lubricating coating has been used in the decorative industries to simulate metallic leaf. More recently a demand has sprung up for metallic powders of nodule-like shape, free of such lubricating coatings, for manufacturing of molded objects. Because of the difference in action of metal in the powder form and in large homogeneous masses an entirely new technique has had to be developed. Any treatment of powdered metal must be of such type as not to interfere with the powdery nature of the material; and this factor has led to considerable difficulties in many instances. Compressibility and a fixed or slight expansion upon sintering of the molded products are desirable.

It has been discovered that the desired expansion on sintering can be obtained by using a highly compressible metal powder. With copper, the principal metal powder in use, a simple standard test has been adopted by some users, which comprises mixing 20 grams of powder and ½% graphite and placing the powder in a mold of 0.20 square inch cross sectional area. The mixture is subjected to a hydraulic pressure of 20,000 pounds per square inch. The height of the molded cylinder should not be over 1.070 inches, as experience has indicated that shrinkage is obtained on sintering a less compressed mass. Lengths from 1.000 to 1.070 are considered good.

Copper powder with sufficient compressibility has been produced by electrolytic deposition of spongy copper. The spongy mass is washed as free as possible of electrolyte and dried under non-oxidizing conditions. It has also been proposed to obtain copper powder by reducing cupric or cuprous oxide powder in a furnace by the use of various reducing gases. The process may be carried out on the furnace hearth, or in trays. The mass that is removed from the furnace in the form of sintered lumps or cakes, is then broken up by milling.

Another method suggested and outlined in the co-pending Drapeau application, Serial Number 3,499, filed January 25, 1935, comprises the reduction of copper oxide powder at low temperatures, of the order of 350° to 750° F., with reducing gas, while subjecting the mass to constant agitation, followed by cooling of the reduced powder in the same atmosphere. The raw material should be a copper oxide (preferably cuprous oxide) powder prepared by oxidizing substantially pure copper by roasting; this is essential if the presence of occluded salts is to be avoided, as these cause rapid atmospheric corrosion. By the use of low temperatures, a porous structure is obtained, together with low apparent density and fairly good mechanical properties. The compressibility, however, is not good, the standard molding varying from 1.090 to 1.120 inches.

In our co-pending application, Serial Number 125,304, filed February 11, 1937, we have disclosed that these and other powders may be improved in compressibility and other properties by subjecting them to mechanical deformation, followed by heating in a non-oxidizing atmosphere below the sintering point of the metal to remove the internal stresses set up.

In this heating operation the upper temperature limit is, of course, the point where the metal powder begins to sinter. Likewise, where copper oxide and other oxides are being reduced, even far below the sintering temperature, a certain amount of sintering occurs due to local over heating, particularly between small numbers of individual particles, thereby producing oversized material.

We have discovered that copper and other metal powders may be exposed to heat treatment, with considerably less tendency toward sintering, by the introduction into the powder of a small percentage of some carbonizable liquid or plastic solid which will form a thin film over the metal surfaces and be carbonized in place to produce a metal powder coated with a carbon film.

For example, we prepared a batch of substantially pure cuprous oxide, all passing through a 325 mesh sieve (particles less than 44 micron diameter). This was placed in a revolving drum, and coal gas was passed through, being burnt under the drum to maintain a temperature of 600° F. The reduction was continued for 36 hours, and the charge was then allowed to cool in the reducing atmosphere; it was a somewhat clinkered mass containing less than 0.20% oxygen. The product was given one pass through an impact hammer mill; the powder resulting gave only a 55% yield of material going through a 325 mesh sieve.

We then added 0.10% by weight of 20° Baumé lubricating oil to the same amount of the same cuprous oxide, and made a run which exactly duplicated the original. The resultant product yielded 90% of powder pass through 325 mesh,

indicating considerably less sintering. The copper powder obtained, when viewed under a high powered microscope, showed the presence of carbon on the surface of the particles.

In another example of our invention, we heated 100 pounds of copper powder in a tray, in an atmosphere of city artificial gas consisting largely of hydrogen and carbon monoxide, to improve its compressibility. It was necessary to hold the heat down to 1,500° F., and after a heating period of 60 minutes, sufficient action had taken place to get the desired change in compressibility. Attempts to shorten the time by increasing the temperature were found useless, as the mass sintered to such an extent that the after milling required destroyed the effect of the treatment, or else produced excessive oversize powder which must be rejected in the classification system.

We then blended 0.1% of 20° Baumé lubricating oil with the powder. It was then possible to heat the batch to 1,700° F. at which temperature sufficient compressibility change occurred in 20 minutes. The batch had not sintered, and was in just as good shape as the untreated batch which had been heated to 1,500° F. A microscopic examination disclosed the presence of carbon on the surface of the powder.

The tendency of iron powder to sinter into solid, or semi-solid masses during a reduction of iron oxides to pure iron powder is substantially overcome through the additions of 0.1% of 26° Baumé lubricating oil. This not only substantially eliminates losses of iron powder as coarse oversize product but permits the production of a powder carrying decidedly more lower micron particle size product.

Similarly, we find that presence of these carbonizable liquids to the extent of 0.10% substantially overcomes sintering during heat treatment to improve the compressibility of iron powders.

Certain other favorable characteristics were noted in this use of lubricating oil. The metal powder, when heated in steel containers without the oil, had tended to diffuse into the steel and alloy with it at the elevated temperatures employed. This resulted in a loss of powder yield, and a weakening of the container. The use of oil in the powder prevented this diffusion, as first the oil, and later the carbon, prevented the diffusion.

The type and amount of carbonizable liquid to be added varies with the time and temperature of heat treatment. Obviously, a product volatile at the heating temperature, without carbonization, is valueless. Similarly, the product must have the ability to spread over the individual particles of metal powder in a thin film, before carbonization, or it fails of its purpose. We have found that lubricating oils and greases are particularly suitable addition products. Other products which may be used are vegetable oils such as corn oil, olive oil, cottonseed oil, cocoanut oil, etc.

The amount of product added should be such as to carbonize to substantial completion during the treatment, but there should be sufficient present to insure the presence of carbon on the metal particle surfaces at the end of the reaction. The carbon formed tends to diffuse into the metal particles, and if heating is carried on for a sufficient period to carbonize the liquid and diffuse the carbon formed, the effect of the addition disappears. The carbon formed is an amorphous carbon, since the temperatures employed are well below those at which graphite or graphitic carbon is formed. In the commercial method of making graphite or graphitic carbon from coke the coke is gradually brought up to temperature in an electrical resistance furnace, and held at 2200° C. to 2600° C. for about a week, and then allowed to gradually cool. The presence of substantial quantities of uncarbonized lubricant is, of course, detrimental to the product. We find that amounts of the order of 0.1% of a percent of the metallic powder to be sufficient for the typical reduction on heating process. Much higher amounts should be avoided; if more than 0.25% is allowed to carbonize in the product, a visible darkening of color occurs.

The carbonizable compound need not be thoroughly admixed with the powder before heating. The type of product used becomes very mobile as the heating progresses, and will effectively penetrate the powder mass merely by being smeared about the container.

The carbon coated metal powders obtained show somewhat less tendency to dust than the untreated powders; and the thin film of carbon does not materially affect the color of the product.

While we have shown the preferred uses of our invention, it is obvious that it is applicable to any heating of powdered metal in which the desired end product is discrete particles of metal powder. The invention resides in the heating of the metal powder in the presence of small quantities of carbonizable liquids.

This application is a division of our copending application Serial No. 125,303, filed February 11, 1937.

We claim:

1. In the production of powdered metal in the form of discrete particles, the step which comprises heating the powdered metal in the presence of about 0.25% or less of an organic compound spreadable over the metal particle surfaces, and carbonizable at the heating temperature, to carbonize the organic compound, the time and temperature of the heat treatment being such that sintering of the powder, and diffusion of the carbon into the metal particles is substantially prevented.

2. In the production of powdered copper in the form of discrete particles, the step which comprises heating the powdered copper in the presence of about 0.25% or less of an organic compound spreadable over the copper particle surfaces, and carbonizable at the heating temperature, to carbonize the organic compound, the time and temperature of the heat treatment being such that sintering of the powder, and diffusion of the carbon into the metal particles is substantially prevented.

3. In the production of powdered metal in the form of discrete particles, the step which comprises heating the powdered metal in the presence of 0.25% or less of an organic compound spreadable over the metal particle surfaces, and carbonizable at the heating temperature.

4. In the production of powdered copper in the form of discrete particles, the step which comprises heating the powdered copper in the presence of 0.25% or less of an organic compound spreadable over the copper particle surfaces and carbonizable at the heating temperatures.

5. The method of producing powdered metal from powdered metal oxides, which comprises reducing the oxide in a reducing gas at an elevated temperature, in the presence of about 0.25% or less of an organic compound spreadable over the

metal particle surfaces and carbonizable at the reducing temperature, to carbonize the organic compound, the time and temperature of the heat treatment being such that sintering of the powder, and diffusion of the carbon into the metal particles is substantially prevented.

6. The method of producing powdered copper from powdered copper oxides, which comprises reducing the oxide in a reducing gas at an elevated temperature, in the presence of about 0.25% or less of an organic compound spreadable over the copper particle surfaces and carbonizable at the reducing temperature, to carbonize the organic compound, the time and temperature of the heat treatment being such that sintering of the powder, and diffusion of the carbon into the metal particles is substantially prevented.

7. The method of improving the compressibility of a powdered metal which comprises heating the powder in a non-oxidizing atmosphere below its sintering point, in the presence of about 0.25% or less of an organic compound spreadable over the metal particle surfaces and carbonizable at the temperature of heating, to carbonize the organic compound, the time and temperature of the heat treatment being such that sintering of the powder, and diffusion of the carbon into the metal particles is substantially prevented.

8. The method of improving the compressibility of a powdered copper which comprises heating the powder in a non-oxidizing atmosphere below its sintering point, in the presence of about 0.25% or less of an organic compound spreadable over the copper particle surfaces and carbonizable at the temperature of heating, to carbonize the organic compound, the time and temperature of the heat treatment being such that sintering of the powder, and diffusion of the carbon into the metal particles is substantially prevented.

9. In a method for preparing metal powders involving a heat treatment of the powdered metallic material used in the process to prepare the final powder, said powdered metallic material being selected from the class consisting of metal powders and powdered oxides of reducible metals, the step comprising heating the powdered material under reducing conditions in the presence of about 0.25% or less of an organic compound spreadable over the particles of the metal powder and carbonizable at the heating temperature whereby sintering is retarded, to carbonize the organic compound, the time and temperature of the heat treatment being such that sintering of the powder, and diffusion of the carbon into the metal particles is substantially prevented.

10. In the production of powdered metal in the form of discrete particles the step which comprises heating powdered metallic material selected from the class consisting of metal powder and powdered oxides of reducible metals under reducing conditions in the presence of 0.25% or less of an organic compound spreadable over the metal particle surfaces and carbonizable at the reducing temperature.

11. The method of producing powdered metal from powdered metal oxides which comprises reducing the oxide in a reducing gas at an elevated temperature in the presence of 0.25% or less of an organic compound spreadable over the surface of the metal particles and carbonizable at the heating temperatures.

JOSEPH E. DRAPEAU, JR.
LOUIS G. KLINKER.

BEST AVAILABLE COPY