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3,520,676 STABILIZATION OF PYROPHORIC METAL POWDER

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8 Claims

ABSTRACT OF THE DISCLOSURE

Pyrophoric powder of metals (such as iron, cobalt, nickel and alloys thereof) is stabilized to prevent its spontaneous ignition. Such stabilization is achieved by wetting the metal particles with a high-boiling organic liquid (such as an ester of carboxylic acid, mineral oil, silicone oil or fatty acid) and holding the wetted particles in the presence of oxygen until a thin oxide layer is formed on the surfaces thereof.

This is a continuation-in-part of my application Ser. No. 650,604, filed July 3, 1967, and now abandoned.

This invention relates to the stabilization of finely divided metal powders to prevent spontaneous ignition thereof, and more particularly, to a process for stabilizing the normally pyrophoric powders of magnetizable metals or metal alloys without adversely affecting the magnetic properties of the treated material.

Finely divided metal powders have increasingly wide usage in many areas of manufacture, e.g., being compacted to form magnets and other metal articles, used as chemical reactants, and as magnetically responsive materials in the manufacture of magnetic tapes and other magnetic recording layers. Iron, nickel, cobalt, or alloys containing two or more of these metals, may be used in the preparation of magnetic tapes, and for such use it is necessary that the individual metal particles be very small in order to provide sufficient information packing density in the recording medium to assure satisfactory reproduction of high frequency signals. Such metals generally oxidize at relatively slow rates, but when prepared in finely divided form, there is such a tremendous increase in the percentage of surface area available for oxidation that these metals become "normally pyrophoric," i.e., they combine so readily with oxygen in the air that spontaneous ignition of the material often results.

Basically, two general processes may be used to passivate (i.e., stabilize) such finely divided metal powders, namely, either the particles may be given permanent coatings of organic materials, or the particle surfaces are oxidized. While a great many variations of these basic passivating processes are well known, these prior art methods are all far from satisfactory in relation to the manufacture of very fine powders, and they are particularly unsatisfactory for use in preparation of the extremely small magnetic particles required for high-resolution recording tapes. Known processes for applying permanent coatings of organic materials have resulted in powders in which magnetic properties (such as saturation induction, remanence and coercivity) are considerably inferior to those of powders without such organic coatings. In addition, organic coatings increase the tendency for the particles to lump together, a serious problem where quality control is important. The prior

art methods for oxidizing the particle surfaces of metal powders, e.g., holding powder in a nitrogen atmosphere and then introducing small quantities of oxygen, do not permit satisfactory control over the thickness of such oxide layers, and the particles treated in this manner have non-uniform oxide layers which severely degrade their magnetic properties.

While it can be readily appreciated that it is essential to passivate normally pyrophoric metal powders so they will not spontaneously ignite on exposure to air, it is also essential that such stabilization be accomplished without substantially disturbing those properties of the metal essential to the purpose for which it is intended.

Accordingly, it is the object of this invention to provide a method for passivating normally pyrophoric metal powders so that they can be safely handled in air without deleteriously affecting the essential properties of the metal. More particularly, an object of the method disclosed herein is to stabilize magnetizable metal powder against spontaneous ignition in air without seriously degrading the magnetic properties of the metal.

These and other objects of the invention herein are accomplished by wetting the normally pyrophoric metal particles with a non-oxidizing organic liquid which is chemically inert to the metal being treated, and thereafter exposing the wetted particles to an oxygen-containing atmosphere. The organic liquid has sufficient viscosity to wet the particles and to separate them. When the wetted particles are exposed to oxygen, it diffuses slowly through the liquid to gain relatively limited but uniform access to the surfaces of the particles, thereby providing the particles with an extremely thin protective oxide coating. Thereafter, the residual organic liquid may be rinsed from the metal particles by a suitable solvent.

Since the physical properties of the wetting liquid required for the relatively simple process just described above are shared by a wide variety of organic materials, many different organic compounds and many different mixtures of compounds of the same or different chemical classes can be used. Essentially, the liquid must have a limited permeability to, or solubility for, oxygen, while being chemically inert to such permeating oxygen and, obviously, to the particular metal powder being treated. Viscosity, of course, must be sufficient to uniformly wet all particle surfaces, to keep the particles separated so that the oxygen will have relatively uniform access to all particle surfaces, and to preclude the possibility that the liquid might flow from the particle surfaces before stabilization is complete. In addition, since the oxidizing reaction often produces considerable heat, it is advantageous to select organic liquids having relatively high boiling points.

Based upon the above requirements, selection of organic liquids for practice of the subject invention should be limited to those materials which are substantially free of oxidizing groups such as nitro groups, sulfate groups, cyano groups, thiocarbonyl groups and substantially free of functional groups which are known to be sequestering. As noted above, these limitations still leave a wide variety of non-oxidizing organic materials which are chemically inert to the metals being treated and of appropriate viscosity. Representative examples of such suitable organic materials are hydrocarbons (e.g., mineral oils, dodecane, tetrahydronaphthalene—Tetralin), triglycerides (e.g., lard oil, sperm oil, olive oil), fatty acids (e.g., steric acid, oleic acid), esters of mineral acids (e.g., tricresyl phosphate, diethyl sulfate), esters of carboxylic acids (e.g., dioctyl phthalate, methyl oleate), mono- and polyhydroxy alcohols (e.g., n-octanol, dodecyl alcohol, ethylene glycol, glycerol); ethers (e.g., 2-ethoxyethanol, dipropylene glycol), polyalkylene glycols (e.g., "Carbowax" from

Union Carbide), silicones (e.g., polymeric dimethyl siloxane, Dow Corning 704), amides (e.g., N,N-dimethyl formamide, N,N-dibutyl formamide), ketones (e.g., cyclopentanone, 2,4-dimethylbenzophenone), and mixtures thereof.

It will be appreciated by those skilled in the art that no ranges of viscosity, oxygen permeability, boiling point, etc. can be arbitrarily set in defining suitable wetting liquids, since the acceptable range of such properties will be found to vary widely and can only be determined in accordance with the particular manner in which this novel process is to be practiced. For instance, viscosity and oxygen permeability requirements can only be empirically determined by several variables, e.g., by the size and amount of the particles being treated, the time which can be allotted for the oxidation reaction, the speed at which particle wetting must take place, solvents available for rinsing purposes, etc., while acceptable boiling points depend on the temperature of the particles when the wetting liquid is to be introduced, the heat expected from the oxidation reaction, etc.

As noted above, the process disclosed herein has particular usefulness in the stabilization of metal powders used in the production of magnetic tapes and other magnetic recording materials. While extremely fine metal powders oxidized by prior art methods are often severely degraded as to the magnetic properties necessary for high quality recording use, such as, coercivity (H_c), maximum flux density (ϕ_m), and squareness (ϕ_r/ϕ_m), it has been found that such powders passivated according to the invention herein can be safely handled in air and yet do not suffer any appreciable loss of these important magnetic properties.

In carrying out the process disclosed herein, it is preferred that the wetted particles be held in a suitable heat-conducting vessel cooled by indirect heat exchange with a cooling fluid, such as chilled water, flowing at such a rate that the reaction temperature in the material being passivated is maintained within an appropriate range, e.g., 20–40° C. for iron. That is, it should be apparent that until stabilization is complete as indicated by cessation of heat generated by the oxidation reaction, the wetted particles should be maintained at a temperature below the ignition temperature of either the particles themselves or of the organic material used to wet them.

Further, the process herein is preferably coordinated with the initial preparation of the metal powder so that the particles will be stabilized immediately for safe handling and storage in air. For instance, metal alloy powders are often produced by coprecipitation of a selection of mixed metal salts, e.g., salts of iron, cobalt and nickel, with oxalic acid. The precipitate, after being washed, filtered and dried, is reduced by passing hydrogen through a combustion tube furnace at temperatures of from 400–450° C. for an hour. The alloy particles are thereafter cooled in nitrogen. At this point in the production of such metal alloy powders, the process disclosed herein is carried out. That is, as soon as the particles are cooled, and while they remain in the nitrogen atmosphere, they are wet with a high-boiling organic liquid, such as any of those referred to above, and thereafter moved to a suitable vessel for exposure to an oxygen-containing atmosphere until passivation is completed in the manner described above.

Similarly, the subject method may be practiced at the end of the well-known process for preparing iron powder by reduction of an iron salt, such as ferrous sulfate, by potassium borohydride, in an aqueous solution. Immediately following the basic reduction step of this well-known process, the iron particles are separated from the water by filtration, and then cleaned by rapid washing in several changes of water. The water is thereafter removed by a first rinsing with a water-miscible organic solvent, such as acetone, and then, after the first solvent is filtered off, by a second rinsing with a water-immiscible organic

solvent for the first solvent, e.g., toluene. At this point in the preparation of the iron particles, powder stabilization may be achieved in accordance with the invention herein, namely, by introducing the high-boiling organic liquid while the particles are still wet with the toluene. However, the oxygen-containing atmosphere is not introduced until sufficient time has elapsed to allow for evaporation of the toluene and the evolution of hydrogen gas which accompanies such borohydride iron reduction.

Therefore, it can be seen that persons skilled in the art can easily coordinate the novel stabilization process disclosed herein with known methods for producing metal powders to passivate immediately such normally pyrophoric materials.

Although the oxygen-containing atmosphere required for the oxidation step in the disclosed process can comprise oxygen in admixture with any inert diluent, it is usually convenient to employ air, or air diluted with nitrogen at normal atmospheric pressure. Of course, pressures above or below normal atmospheric pressure can be employed. Also, while the oxygen-containing gaseous mixture can be passed through the wetted-particle slurry in any convenient manner, when the stabilized powder is to be used in the manufacture of magnetic tape, it has been found preferable to agitate or stir the wetted particles in the presence of the oxygen atmosphere to assure that the individual particles will be oxidized at a substantially uniform rate and to a substantially uniform degree.

After stabilization is complete, residual organic material may be rinsed from the metal particles by any solvent or solvent system which is free of sequestering groups and which may be thereafter removed from the passivated material by evaporation without requiring temperatures high enough to produce deleterious effects on the desired physical properties of the particles. Those skilled in the art will readily appreciate that there are many organic solvents suitable for such rinsing purposes, such as acetone, dichlorethane, ether, toluene, etc.

It is believed that the rather remarkable results obtained by the invention herein are achieved by virtue of the fact that the organic liquid so effectively controls the rate at which the surface of the particles is oxidized that the layer of oxidized metal formed on the surface of each particle is extremely thin and uniform. It has been found that while the oxidized layer produced in accordance with the invention herein satisfactorily stabilizes the metal against ignition in air, the layer itself is so thin that the metal oxide is not detectable by X-ray diffraction analysis. Therefore, the metal oxide formed by the process herein must comprise less than the detectable limits of such X-ray diffraction analysis, namely, less than 5–10% of the particles. Since the oxide forms such a small percentage of the powder, the metal properties of the powder remain substantially unimpaired by the stabilization process. In this regard, it should be noted that when the process is being used to stabilize iron powder for magnetic recording purposes, care should be taken to maintain the particles at the relatively low temperatures referred to above in order to avoid degradation of the magnetic properties of the iron.

Attention is also called to the fact that the time required for stabilization varies widely with different metals and alloys. It has been found that with iron powder the stabilization time can be varied by controlling the density of the oxygen atmosphere and the temperature of the particles, and iron-cobalt-nickel alloy powders can be stabilized very fast without degrading their magnetic properties. In fact, as soon as the latter particles have been wetted, they can be moved to an oxygen atmosphere and immediately filtered, rinsed and dried. Any attempt to handle such particles in this manner without first wetting them in accordance with the invention herein generally results in the spontaneous ignition of this material.

The invention is further illustrated by the following examples.

5 EXAMPLE 1

(A) Iron powder is first prepared by small scale borohydride reduction in the following manner: a 3 liter water solution of 1 M potassium borohydride is added dropwise to 3 liters of 1 M aqueous ferrous sulfate solution contained in a shallow dish over an array of U-shaped magnets. A twenty-minute period is then allowed for the reaction to go to completion. The iron powder resulting from the reaction is collected by suction filtration and washed with freshly boiled water which is essentially air-free. The powder is next washed, first with acetone and then with toluene, and thereafter filtered. After the toluene wash and prior to evaporation of the toluene, the iron powder is divided into two equal portions.

(B) A first portion is immediately immersed in 2 liters of dioctyl phthalate. After allowing this first portion to stand for several hours in the dioctyl phthalate to permit evaporation of residual toluene and liberation of absorbed hydrogen, the powder is filtered from the dioctyl phthalate and then placed in an open, water-jacketed, stainless steel tray. Cooling water is circulated through the water jacket at a rate such that exit water is maintained about 5° C., keeping the iron temperature between 25 and 30° C. The particles are stirred, and after it is observed that liberation of sensible heat has stopped, the residual dioctyl phthalate is removed from the powder by washing with toluene and acetone. The powder is then allowed to dry at room temperature. About 75 grams of non-pyrophoric, stable, strongly ferromagnetic black iron powder is recovered, having no detectable amount of iron oxide by X-ray diffraction analysis (detectable limits within 5–10%). The iron powder has the following magnetic properties (for a measuring field strength of 1,000 oersteds): $H_c=420$ oersteds, $\phi m=4.95$ maxwells, $\phi r/\phi m=66.7\%$. The test samples are 1/4-inch-diameter cylindrical cured plastisols having an iron content of 4% by weight.

(C) The second portion of iron powder is not treated with dioctyl phthalate. It ignites spontaneously in the air following evaporation of the toluene.

EXAMPLE 2

The procedure of Example 1(B) is followed, with the exception that light mineral oil is used in place of the dioctyl phthalate. Similar inhibition of spontaneous combustion results. The iron powder has the following magnetic properties: $H_c=415$ oersteds, $\phi m=3.25$ maxwells, $\phi r/\phi m=53.8\%$.

EXAMPLE 3

A powder of $Fe_{0.55}Co_{0.40}Ni_{0.05}C_2O_4 \cdot H_2O$ is prepared in the following manner: To a solution of 612 grams of $FeSO_4 \cdot 7H_2O$, 450 grams of $CoSO_4 \cdot 7H_2O$, and 52.6 grams of $NiSO_4 \cdot 6H_2O$ dissolved in 8 liters of water contained in a 14-liter vessel is added, with rapid stirring, 600 grams of $(NH_4)_2C_2O_4 \cdot H_2O$, suspended in 6 liters of water. The product is stirred for 15 minutes then washed several times with water and filtered. The residue is washed with acetone and dried in air. Eighty grams of the oxalate prepared as described above is reduced by hydrogen in a combustion tube furnace maintained at 400–450° C. Reduction is carried out for one hour. The resulting finely divided Fe-Co-Ni alloy particles are cooled in the cool section of the combustion tube in a nitrogen atmosphere. While still in the nitrogen atmosphere, the particles are placed in a bath of light silicone oil (polymeric dimethylsiloxane, Dow Corning 704). The wetted particles are then removed from the nitrogen atmosphere to air and immediately filtered and washed with toluene. No heating of the dried particles is observed, and no pyrophoric ignition occurs. The particles exhibit very good magnetic properties for high-resolution recording tape use.

6 EXAMPLE 4

The procedure of Example 1(B) is followed, using oleic acid as the wetting liquid. Similar inhibition of spontaneous combustion results. The particles exhibit good magnetic properties.

EXAMPLE 5

The procedure of Example 3 is followed, using diethyl sulfate as the wetting liquid. Similar inhibition of spontaneous combustion results. The particles exhibit good magnetic properties.

EXAMPLE 6

The procedure of Example 1(B) is followed, using ethylene glycol as the wetting liquid. Similar inhibition of spontaneous combustion results. The particles exhibit good magnetic properties.

EXAMPLE 7

The procedure of Examples 3 is followed using di-propylene glycol as the wetting liquid. Similar inhibition of spontaneous combustion results. The particles exhibit good magnetic properties.

EXAMPLE 8

The procedure of Example 1(B) is followed using "Carbowax" as the wetting liquid. Similar inhibition of spontaneous combustion results. The particles exhibit good magnetic properties.

EXAMPLE 9

The procedure of Example 3 is followed using N,N-dimethyl formamide as the wetting liquid. Similar inhibition of spontaneous combustion results. The particles exhibit good magnetic properties.

EXAMPLE 10

The procedure of Example 3 is followed using cyclopentanone as the wetting liquid. Similar inhibition of spontaneous combustion results. The particles exhibit good magnetic properties.

Although the invention has been described in detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications may be incorporated without departing from the spirit and scope of the invention.

I claim:

1. A method for stabilizing normally pyrophoric metal powder comprising:
 - 50 wetting the individual particles of such powder with a high-boiling organic liquid which permits oxygen to diffuse slowly therethrough, said liquid being substantially chemically inert to said metal and to said diffusing oxygen, and
 - 55 holding the particles so wetted in the presence of oxygen until liberation of sensible heat has stopped, thereby forming an extremely thin oxide layer (less than 5–10% by volume) on the surface of each particle.
2. The method according to claim 1 wherein said particles are agitated or stirred during said holding step.
3. The method according to claim 1 wherein said particles are cooled during said holding step to remove heat generated by the reaction of said particles with oxygen.
4. The method according to claim 1 wherein said process comprises the additional step of removing said organic liquid from said surface-oxidized particles by washing in an evaporatable solvent for said liquid.
5. The method according to claim 1 wherein said metal powder is selected from the group consisting of iron, cobalt, nickel and alloys thereof.
6. The method according to claim 1 wherein said organic liquid is selected from the group consisting of hydrocarbons, fatty acids, esters of mineral or carboxylic

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acids, mono- and polyhydric alcohols, ethers, polyalkylene glycols, silicones, phenols, amides, ketones and mixtures thereof.

7. The method according to claim 4 wherein said solvent is selected from the group consisting of acetone, dichloroethane, ether and toluene.

8. A method of stabilizing a normally pyrophoric metal powder selected from the group consisting of iron, cobalt, nickel and alloys thereof, following preparation of said powder and cooling thereof in an oxygen-free atmosphere, said method comprising:

immersing said powder while still in said oxygen-free atmosphere with mineral oil,

filtering said powder and placing it in a heat-conducting vessel cooled by indirect heat exchange,

holding said powder in said vessel in the presence of air,

stirring said powder until liberation of sensible heat

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has ceased, and thereafter washing said powder with toluene and then acetone to remove residual mineral oil therefrom.

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