United States Patent Office 3,574,683
Patented Apr. 13, 1971

3,574,683

PREPARATION OF MAGNETIC PARTICLES BY REACTING IRON, COBALT, OR NICKEL SALTS WITH PHTHALATE ION IN DIALKYL SULFOXIDE

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No Drawing. Filed Jan. 14, 1969, Ser. No. 793,196
Int. Cl. H01f 10/00; C22b 23/04
U.S. Cl. 117—235 12 Claims

ABSTRACT OF THE DISCLOSURE

A method for preparing finely divided magnetic metal particles by dissolving a metal salt of nickel, cobalt, iron, or mixtures of these in a dialkyl sulfoxide bath, preferably dimethyl sulfoxide; reacting with phthalate ion in said bath; precipitating the metal phthalate reaction product by adding water to the bath; separating the precipitate; heating and reducing with hydrogen at elevated temperatures to produce metallic particles of cubic structure in a fine particle size range of about .01 micron to about 7 microns, which are useful in magnetic recording media and for preparing permanent magnets, magnetic cores, and magnetically responsive fluid compositions as are employed in magnetic clutches and the like. Precipitation of the metal phthalate is not achieved if aqueous solutions of metal salt and phthalate ion are mixed and dialkyl sulfoxide is added thereafter.

FIELD OF THE INVENTION

This invention relates to the manufacture of fine magnetic particles suitable for use in magnetic recording media, permanent magnets, magnetic cores, and in magnetically responsive fluid suspensions, such as magnetic or electrostrictive clutch coupling and the like.

SUMMARY OF THE INVENTION

More particularly, the invention relates to a method of making fine magnetic metal, alloy, or oxide particles by dissolving a metal salt of nickel, cobalt, iron, or mixtures of these salts in a dialkyl sulfoxide bath (preferably dimethyl sulfoxide); reacting the metal salt with phthalate ion which is dissolved in the dialkyl sulfoxide bath; precipitating the metal phthalate reaction product by adding water to the bath; separating the precipitate; and decomposing the precipitate, either by heating in an oxidizing atmosphere at 100–450° C. for a period of time sufficient to remove organic matter and provide a magnetic oxide, or by reducing the precipitate or the oxide formed by the precipitate with hydrogen at elevated temperatures to produce metallic particles of cubic structure in fine particle size varying between about 0.01 micron to about 7 microns.

During the water dilution-precipitation step which follows the combination of phthalate ion and metal salt in the dialkyl sulfoxide bath, it may be advantageous to employ an ultrasonic field which aids in crystallizing single metal salts or co-crystallizing mixtures of metal salts and in producing the metal phthalate in very fine and uniform particle size range which, in turn, leads to superior magnetic results.

The ultrasonic field may be formed by commercially available devices, such as the "Rapisonic" ultrasonic device sold by Sonic Engineering Corporation, Stamford, Conn., which vibrates a blade at a frequency of 22K c.p.s., or by piezoelectric crystal transducers (e.g., quartz, barium titanate, and the like which convert electric energy into ultrasonic waves between 10K c.p.s. and 1M c.p.s.), or by other transducers which are described in the literature. Low intensities of the order of .01—0.7 watt per square centimeter of ultrasonic energy are generally adequate to disperse the precipitate and prevent particle agglomeration by vibrational motion in the dialkyl sulfoxide bath.

The phthalate ion may conveniently be provided from monobasic soluble salts of phthalic acid, such as sodium acid phthalate, potassium acid phthalate, ammonium acid phthalate; from soluble dibasic salts of phthalic acid, such as disodium phthalate, dipotassium phthalate, diammonium phthalate; from phthalic anhydride; or from phthalic acid.

Any soluble salt of iron, cobalt, or nickel may be used, and the chlorides, nitrates, sulfates, and acetates are representative salts which are readily available and have been used with good results.

It is preferred to use a dilute solution of a metal salt in a dialkyl sulfoxide bath and to add the phthalate to it in diluted form, also in dialkyl sulfoxide. For convenience and easy control, fractional molar quantities are mixed by preparing separate solutions of salt in dialkyl sulfoxide and of phthalate ion in dialkyl sulfoxide.

If similar amounts of metal salt or of phthalate ion are dissolved in water instead of in dialkyl sulfoxide and mixed, no precipitation is observed. If the same amount of dialkyl sulfoxide is added to such a water solution as was used in the method of the invention, there is no change and no precipitation occurs.

In short, an essential feature of the method of the present invention is the dialkyl sulfoxide bath as the medium for dissolving the metal salt and phthalate ion in the sequence of first dissolving and then precipitating the metal phthalate by adding water.

For reasons of economy and availability, dimethyl sulfoxide is the preferred dialkyl sulfoxide, but diethyl sulfoxide, dipropyl sulfoxide, dibutyl sulfoxide, and diisobutyl sulfoxide may be used. Unsymmetrical sulfoxides may be used, such as methyl ethyl sulfoxide and methyl isobutyl sulfoxide.

The foregoing and other objects, features, and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples are given by way of pointing out critical aspects of the invention and preferred embodiments.

Example 1A.—Criticality of dialkyl sulfoxide bath as the medium for reacting phthalate ion and metal salt in the absence of water

Solutions of one-tenth molar

$$CoCl_2 \cdot 6H_2O \text{ and } FeCl_2 \cdot 4H_2O$$

in water and in dimethyl sulfoxide were prepared.

One-tenth molar solutions of potassium acid phthalate in water and in dimethyl sulfoxide were prepared.

Equal volumes of the above 0.1 molar ferrous chloride in water and 0.1 molar phthalate solution in water were mixed. No precipitation was observed.

A volume of dimethyl sulfoxide equal to that of the 0.1 molar ferrous chloride and 0.1 molar potassium acid phthalate was added to the aqueous mixture and no precipitation was observed.

Equal volumes of the above 0.1 molar ferrous chloride in dimethyl sulfoxide and 0.1 molar potassium acid phthalate in dimethyl sulfoxide were mixed. No precipitate was formed. A volume of water twice that of the volume of ferrous chloride and potassium acid phthalate solution was added and the solution was agitated manually, and the metal phthalate salt precipitated.

A mixture of equal parts by volume of 0.1 molar cobalt chloride in dimethyl sulfoxide and 0.1 molar ferrous chloride in dimethyl sulfoxide was reacted with an equal volume of 0.1 molar potassium acid phthalate salt and the co-crystallized cobalt-iron phthalates were precipitated by adding water in a volume equal to the volume of the reaction mixture.

The iron phthalate salt and the mixed iron-cobalt phthalate salt prepared above were separated by filtration and the residue was washed with water and placed in an oxidizing atmosphere in a furnace at 400° C. for 3 hours. In each instance, all of the organic matter of the precipitate was removed and a finely divided magnetic oxide was obtained; e.g., iron oxide in the form of black gamma iron oxide, and black flakes of cobalt-modified oxide, respectively.

These two magnetic oxide samples were then placed in a furnace maintained at a temperature of 260° C. and hydrogen reducing gas was passed over them for 2 hours to convert the oxide particles to the corresponding metal and alloy particles. All of the reduced particles were magnetic, cubic in shape, and ranged in size from about 0.01 to about 6.1 microns.

Example 1B.—Effect of ultrasonic vibrations on diminishing size of resulting magnetic oxide and metal particles

The precipitations in dimethyl sulfoxide of the two samples of salts as above (iron and iron-cobalt mixture) were repeated, using an 800 k.c. quartz piezoelectric transducer to provide an ultrasound field during the dilution-precipitation step. The resulting oxide particles, after heating in the furnace, were much smaller than those which had been produced in the absence of the ultrasonic field. After hydrogen reduction at 260° C. for 2 hours, as above, the particle size ranged from 0.01 to 1.0 micron. The average particle size of the iron particles was 0.03 micron, and the average particle size for the mixed iron-cobalt particles was 0.04 micron.

Example 2.—Effect of variations in concentration of metal salt solutions in dimethyl sulfoxide

This example illustrates the doubling of the metal salt concentration from 0.1 molar to 0.2 molar. The beneficial results of this example are achieved with increasing concentrations as high as 0.9 molar. At higher concentrations, additional washing is necessary and control of uniformity of particle size is more difficult to maintain under conditions of normal manual agitation.

In general, the same procedure was followed as in Example 1A above and 8 g. of $FeCl_2.4H_2O$ were dissolved in 200 ml. of dimethyl sulfoxide to form a 0.2 molar solution. Eight g. of potassium acid phthalate were dissolved in 200 ml. of dimethyl sulfoxide to form a 0.2 molar solution. These solutions were mixed and no reaction occurred. 300 ml. of distilled water was added, causing precipitate to form which was allowed to settle overnight. The supernatant liquid was siphoned off and the precipitate washed with 1000 ml. of distilled water. This washing procedure was repeated six times and the precipitate was then removed by centrifuging, dried at 100° C. for 54 hours, and then reduced in a nickel boat under hydrogen at 400° C. for 2 hours. The metal particles recovered were cubic in form, varied in particle size between 0.01 and 0.1 micron, and had an average particle size of 0.03 micron.

The following magnetic properties were observed when run on the Vibrating Sample Magnetometer (VSM) at an applied field strength of 4000 oersteds:

Ms 4000 oe.—134 emu. (electromagnetic units per g.)
Hc—547 oe.
Mr/Ms [1]—0.33

[1] Squareness ratio.

Example 3.—Preparation of mixed cobalt-iron magnetic particles

A 0.2 molar solution of mixed cobalt and iron salts was prepared by dissolving 9.6 g. of $CoCl_2.6H_2O$ and 8.0 g. of $FeCl_2.4H_2O$ in 200 ml. of dimethyl sulfoxide. A 0.2 molar phthalate solution was prepared by dissolving 12 g. of potassium acid phthalate in 300 ml. of dimethyl sulfoxide. The mixed salts in solution were added without reaction to the phthalate solution with efficient agitation, and 800 ml. of distilled water was then added to cause precipitation. The precipitate was allowed to settle; the supernatant liquid was siphoned off; and the material was washed six times with distilled water, 1000 ml. of distilled water being used in each washing. After the sixth washing, the wet concentrated water slurry was centrifuged and the precipitate was removed and dried at 100° C. for 54 hours. The product was then put in a nickel boat, reduced at 400° C. under hydrogen for 2 hours, and cubic crystals of magnetic cobalt-iron in a particle size range of from 0.02 to 5.8 microns were produced. The average particle size was 1.5 microns. By testing on the VSM, the following magnetic characteristics were determined:

Ms 4000 oe.—167 emu.
Hc—226 oe.
Mr/Ms—0.12

Example 4.—Preparation of mixed nickel-iron magnetic particles

A 0.2 molar solution of mixed nickel and iron salts was prepared by dissolving 9.6 g. of $NiCl_2.6H_2O$ and 8 g. of $FeCl_2.4H_2O$ in 200 ml. of dimethyl sulfoxide. A 0.2 molar solution of phthalate was prepared by dissolving 12 g. of potassium acid phthalate in 300 ml. of dimethyl sulfoxide. The mixed salts in solution were added without reaction to the phthalate solution with efficient agitation, and 800 ml. of distilled water was then added to cause precipitation. The precipitate was allowed to settle; the supernatant liquid was siphoned off; and the material was washed six times with distilled water, 1000 ml. of distilled water being used in each washing. After the sixth washing, the wet concentrated water slurry was centrifuged and the precipitate was removed and dried at 100° C. for 54 hours. The product was then put in a nickel boat, reduced at 400° C. under hydrogen for 2 hours, and cubic crystals of magnetic nickel-iron in a particle size range of 0.01 to 0.5 micron were produced. The average particle size was 0.1 micron. By testing on the VSM, the following magnetic characteristics were determined:

Ms 4000 oe.—175 emu.
Hc—196 oe.
Mr/Ms—0.1

Example 5.—Addition of powdered phthalic acid to dimethyl sulfoxide

A 0.2 molar solution of mixed nickel and iron salts was prepared by dissolving 9.6 g. of $NiCl_2.6H_2O$ and 8 g. of $FeCl_2.4H_2O$ in 200 ml. of dimethyl sulfoxide. 16 g. of powdered phthalic acid was added to the solution of nickel and iron salts in the dimethyl sulfoxide bath with agitation. No precipitate formed.

There was then added 1800 ml. of distilled water to cause precipitation. The precipitate was allowed to settle; the supernatant liquid was siphoned off; and the material was washed six times with distilled water, 1000 ml. of distilled water being used in each washing. After the sixth washing, the wet concentrated water slurry was centrifuged and the precipitate was removed and dried at 100° C. for 54 hours. The product was then put in a nickel boat, reduced at 400° C. under hydrogen for 2 hours, and cubic crystals of magnetic nickel-iron in a particle size range of 0.01 to 0.1 micron were produced.

The average particle size was 0.04 micron. By testing on the VSM, the following magnetic characteristics were determined:

Ms 4000 oe.—159 emu.
H_2—463 oe.
Mr/Ms—0.3

Example 6—Preparation of 70% iron—30% cobalt

A 0.1 molar solution of 70:30 iron-cobalt was prepared by dissolving 6.73 g. $FeCl_2.4H_2O$ and 3.27 g. of

$CoCl_2.6H2O$

in 500 ml. of dimethyl sulfoxide. A 0.1 molarphthalate ion solution was prepared by dissolving 10.2 g. of monopotassium phthalte in 500 ml. of dimethyl sulfoxide. These 500 ml. solutions were mixed together without reaction, and 1000 ml. of distilled water was added while agitating to cause precipitation. An additional 1000 ml. was added to insure complete precipitation. The precipitate was alloweed to settle; the supernatant liquid was siphoned off; and the material was washed twice with distilled water, 1000 ml. of distilled water being used in each washing. After the second washing, the concentrated water slurry was centrifuged and the precipitate was removed. The product was heated at 400° C. 14 hours, whereby organic matter was eliminated and a magnetic cobalt modified iron oxide was produced. The magnetic oxide was reduced in a furnace at 260° C. with hydrogen for 2 hours and the resulting alloy had the following magnetic characteristics:

Ms 4000 oe.—109 emu.
Hc—303 oe.

Example 7.—Preparation of 60% iron—40% cobalt

A 0.1 molar solution was prepared by dissolving 6.05 g. of $FeCl_2.4H_2O$ and 4.59 g. of $CoCl_2.6H_2O$ in 500 ml. of dimethyl sulfoxide. A 0.1 molar solution of phthalate ion was prepared by dissolving 10.2 g. of potassium acid phthalate in 500 ml. of dimethyl sulfoxide. These 500 ml. solutions were mixed togeher without reaction and 1000 ml. of distilled water was added while agitating to cause precipitation. An additional 1000 ml. of distilled water was added to insure complete precipitation. The precipitate was allowed to settle; the supernatant liquid was siphoned off; and the material was washed twice with distilled water, 1000 ml. of distilled water being used in each washing. After the second washing, the concentrated water slurry was centrifuged and the precipitate was removed. The product was heated at 400° C. 14 hours, whereby organic matter was eliminated and a magnetic cobalt modified iron oxide was produced. The magnetic oxide was reduced in a furnace at 260° C. with hydrogen for 2 hours to produce a magnetic alloy.

Example 8.—Preparation of magnesium modified ironparticles with phthalic acid addition

In 200 ml. of dimethyl sulfoxide, there were dissolved without reaction 16 g. of $FeCl_2.4H_2O$, 4 g. of

$MgCl_2.6H_2O$

and 16 g. of phthalic acid. A volume of distilled water which was five times that of the dimethyl sulfoxide (e.g., 1000 ml.), was added with agitation to cause precipitation. The precepitate was washed and the wash liquor was removed by siphoning and centrifuging. The centrifuged material was again washed and dried overnight in an oven at 100° C., and reduced with hydrogen in a tube furnace at 400° C. for 2 hours to produce a magnetic alloy of iron and magnesium.

Example 9.—Preparation of iron-cobalt-magnesium particles with phthalic acid addition

In 200 ml. of dimethyl sulfoxide, there were dissolved without reaction 8 g. of $FeCl_2.4H_2O$, 9.6 g. of

$CoCl_2.6H_2O$

4 g. $MgCl_2.6H_2O$, and 16 g. of phthalic acid. A volume of distilled water which was five times that of the dimethyl sulfoxide (e.g., 1000 ml.) was added with agitation to cause precipitation. The precipitate was washed and the wash liquor was removed by siphoning and centrifuging. The centrifuged material was again washed and dried overnight in an oven at 100° C., and reduced with hydrogen in a tube furnace at 400° C. for 2 hours to produce a magnetic alloy of iron-cobalt-magnesium.

The products from Examples 8 and 9 were combined and gave the following values for the magnetic characteristics:

Ms 4000 oe.—114 emu.
Hc—417 oe.
Mr/Ms—0.23

Example 10.—Iron particles from ferrous sulfate and phthalic acid

To 100 ml. of diethyl sulfoxide, there was added 8 g. of $FeSO_4 \cdot 7H_2O$ and 8 g. of phthalic acid and the solution was mixed for 45 minutes at room temperature without reaction. The solution was diluted with 1000 ml. of distilled water to precipitate the insoluble iron salt which was washed twice with 1000 ml. portions of distilled water, centrifuged, dried at 100° C. overnight, and reduced with hydrogen at 400° C. for 2 hours, whereby cubic crystals of magnetic iron where recovered.

The foregoing examples illustrate the wide range of volume proportions of precipitating water relative to the dialkyl sulfoxide bath; e.g., from proportions of 1:1 to about 10:1. Larger water volumes may be used (in proportions of 20:1, 40:1, 50:1, etc.), but it is obviously impractical and contrary to sound washing practice to employ such a large excess water volume as to risk mechanical loss of the precipitate which is in very finely divided form.

In preparing magnetic recording media, the gamma iron oxide or cobalt modified gamma iron oxide in acicular form obtained when the process as in Example 1A included an oxidation step, but no reduction step, may be used together with a film-forming binder.

Mixtures of iron-cobalt metal particles prepared in Example 1 may be used with a binder in the preparation of magnetic recording media, or the iron particles prepared in Example 2 may be used for sound recording tape and, similarly, the metal particles of the remaining examples are also useful in preparing various recording media; especially the iron-cobalt-nickel particles obtained by mixing the products of Examples 4 and 6.

Typical, but not limiting, binders for these various recording media are polyesters, cellulose esters and ethers, vinyl chloride, vinyl acetate, acrylate and styrene polymers and copolymers, polyurethanes, polyamides, aromatic polycarbonates (as, for example, those produced from 2,2 - bis - (4-hydroxyphenyl)propane), and polyphenyl ethers (as, for example, those produced by oxidative coupling of 2,6 dimethyl phenol).

In addition to dialkyl sulfoxides, a wide variety of solvents may be used for forming a dispersion of the fine particles and binders. Organic solvents, such as ethyl, butyl and amyl acetate, isopropyl alcohol, dioxane, acetone, methylisobutyl ketone, cyclohexanone, and toluene frequently are used for this purpose. The particle-binder dispersion may be applied to a suitable substrate by roller coating, gravure coating, knife coating, extrusion or spraying of the mix onto the backing or by other known methods. The specific choice of non-magnetic support, binder, solvent, or method of application of the magnetic particles to the support will vary with the properties desired and the specific form of the magnetic recording medium being produced.

In addition to organic binders, lubricants, such as silicon oil, graphite, molybdenum disulfide, oleyl butyrate ester, oleic acid amide and the like may be used in pre-

paring magnetic record media such as video tapes, computer tapes, and sound tapes.

In preparing recording media, the magnetic particles comprise about 40–90% by weight of the film layer applied to the substrate. The substrate is usually a paper, polyester, or cellulose acetate material, although rigid base material of plastic or metal is more suitable for some uses.

In preparing magnetic cores and permanent magnets, the products of the foregoing examples are mixed with non-magnetic plastic or filler in an amount of 33 to 50% by volume of the finished magnetic metal, the particles aligned in a magnetic field, and the mixture pressed into a firm magnet structure. Alignment of the particles may be accomplished in an externally applied D.C. magnetic field of about 4000 gauss or more, and fields up to 28000 gauss may be used. Pressures may vary widely in forming the magnet, and pressures up to 100,000 p.s.i. have been used commercially.

In preparing fluid magnetic compositions, the magnetic particles prepared in accordance with the invention may be mixed with hydrocarbon mineral oil or with other liquids as disclosed in Winslow, U.S. Pat. 2,417,850, and Rabinow, U.S. Pat. 2,575,360. The oil-diluted magnetic composition responds to a magnetic field and is useful in power couplings and clutches.

While there has been described and pointed out the fundamental novel features of the invention as applied to preferred embodiments, it will be understood that various omissions and substitutions and changes in the form and details of the invention illustrated may be made by those skilled in the art without departing from the spirit of the invention. It is therefore the intention thereof to be limited only as indicated by the scope of the following claims.

What is claimed is:

1. A method for manufacturing magnetic particles comprising:
dissolving salt including a metal salt of nickel, cobalt, iron, and mixtures thereof in a bath containing dialkyl sulfoxide;
reacting with phthalate ion dissolved in said bath;
precipitating the metal phthalate by adding water to the bath;
separating the precipitate; and
reducing the precipitate with a reducing gas at elevated temperatures to recover finely divided metal particles.

2. A method as claimed in claim **1**, wherein said reducing step is carried out at temperatures between about 225 and 450° C. with a reducing gas selected from the group consisting of hydrogen and carbon monoxide and said magnetic particles are produced in the form of crystals of cubic structure in a particle size range of .01 micron to about 7 microns.

3. A method as claimed in claim **1** wherein said salt includes an iron salt.

4. A method as claimed in claim **3** wherein said salt includes a nickel salt.

5. A method as claimed in claim **3** wherein said salt includes a cobalt salt.

6. A method as claimed in claim **1** wherein said phthalate ion is derived from a monobasic salt of phthalic acid.

7. A method as claimed in claim **1** wherein said phthalate ion is derived from phthalic acid.

8. A method as claimed in claim **1** wherein said phthalate ion is derived from phthalic anhydride.

9. A method for manufacturing magnetic oxide particles comprising:
dissolving salt including a metal salt of nickel, cobalt, iron, and mixtures thereof in a bath containing dialkyl sulfoxide;
reacting with phthalate ion dissolved in said bath;
precipitating the metal phthalate by adding water to the bath;
separating the precipitate; and
heating the precipitate at 100–450° C. in the presence of oxygen to remove organic matter.

10. A method as claimed in claim **1** wherein said dialkyl sulfoxide bath consists essentially of dimethyl sulfoxide.

11. A method of manufacturing magnetic recording media comprising:
dissolving salt including a metal salt of nickel, cobalt, iron, and mixtures thereof in a bath containing dialkyl sulfoxide;
reacting with phthalate ion dissolved in said bath;
precipitating the metal phthalate by adding water to the bath;
separating the precipitate;
reducing the precipitate with a reducing gas at elevated temperatures to recover finely divided metal particles;
adding a non-magnetic binder to said magnetic particles in a solvent for the binder to form a dispersion;
coating a base with said dispersion; and
drying the coating.

12. A method of manufacturing magnetic recording media comprising:
dissolving salt including a metal salt of nickel, cobalt, iron and mixtures thereof in a bath containing dialkyl sulfoxide;
reacting with phthalate ion dissolved in said bath;
precipitating the metal phthalate by adding water to the bath;
separating the precipitate;
heating the precipitate at 100–450° C. in the presence of oxygen to remove organic matter;
adding a non-magnetic binder to said magnetic particles in a solvent for the binder to form a dispersion;
coating a base with said dispersion; and
drying the coating.

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U.S. Cl. X.R.

75—0.5AA, 119, 121; 117—240; 148—105; 260—439