

- [54] **COMPOSITION OF METAL SALT CRYSTALS HAVING A POLYMERIC COATING**
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- [58] Field of Search..... 117/100 B, 234, 235; 252/62.54

[56] **References Cited**

UNITED STATES PATENTS

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3,228,882	1/1966	Harle et al.	117/235 X
3,574,685	4/1971	Haines	117/235 X

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[57] **ABSTRACT**

A dry powder like composition formed of a mass of acicular particles of a metal-containing thermally decomposable organic salt crystals having a polymeric coating.

9 Claims, No Drawings

COMPOSITION OF METAL SALT CRYSTALS HAVING A POLYMERIC COATING

RELATED APPLICATION

This is a continuation-in-part of commonly-owned U.S. Ser. No. 127,514, filed 3/24/71 and now abandoned by the same inventors and entitled METALLIC POWDERS AND THEIR PREPARATION.

BACKGROUND OF THE INVENTION

This invention relates to magnetic powders and their preparation. It relates more particularly to very small ferromagnetic particles of cobalt and its alloys and to a method of making same, and to a magnetic recording member having these particles as its magnetic pigment.

Ferromagnetic particles are employed in a variety of applications. For example, in the form of coatings on tapes, cards, drums and disks, they serve as the recording medium for information recorded in magnetic form. They are used also to form magnets. They have further application in connection with microwave circuitry and various electronic equipment.

Ferromagnetic particles of cobalt and cobalt-iron have been known as useful as recording pigments, the particles being produced by a number of old processes. These processes include both the direct chemical reduction of cobalt from an oxide and electrolytic deposition of the metal. Cobalt particles have also been prepared by thermal decomposition of cobalt-containing compounds such as cobalt carbonyl and cobalt oxalate.

The particles produced with these prior techniques do not form a recording pigment having optimum recording characteristics. The sigma value (the intensity of magnetization (M) divided by the density of the material), is too small, i.e., generally less than 60 e.m.u./g. However, because the prior particles oxidize to an appreciable extent and often carry an excessively thick surface coating of a polymer to protect them from further oxidation, the sigma values drop below the 60 e.m.u./g. figure.

Another property which is critical to a high-quality recording medium is its squareness characteristic. Squareness is defined as the ratio of the remanent magnetization (M_r) to the saturation magnetization (M_s). The prior cobalt powders generally have relatively low squareness figures for the bulk material, i.e., less than 0.25.

Furthermore, it has proven difficult to apply these particles to substrates such as tapes so that they are aligned uniformly and are distributed evenly throughout the binder, a practical requirement for high-quality recording. Still further, with respect to the carbonyl process, cost is a negative factor both because of the cost of the carbonyl itself and because of the special precautions that must be taken to handle this extremely poisonous gas.

Cobalt powder has also been prepared by direct reduction from cobalt hydroxide. The cobalt particles are coated with a polymer and in this form they exhibit a high coercive force. The presence of excessive polymer on the particles lowers the sigma value. Also sometimes it reacts adversely with the binder on the substrate. In addition, it has proven difficult to distribute the prior cobalt particulate materials uniformly on the tape substrate and align the particles.

Moreover, it has been found that a number of workers have described methods of making cobalt particles

by the reduction of a cobalt oxalate salt. For example, Haines in U.S. Pat. No. 3,574,685, teaches the formation of a cobalt salt in dimethyl sulfoxide and the subsequent thermal decomposition of the oxalate to form cobalt particles.

As a result of the aforementioned difficulties, cobalt metal particles have not been used as a recording pigment to any great extent. Rather, the industry has turned to the metal oxides such as iron oxides.

SUMMARY OF THE INVENTION

Accordingly, this invention aims to provide magnetic cobalt-containing particles having superior magnetic characteristics which enable them to be used as a high-quality magnetic recording pigment.

Another object of the invention is to provide single domain cobalt and cobalt-containing particles.

A further object of the invention is to provide cobalt and cobalt-containing particles which are characterized by minimum resistance to dispersion in organic matrices such as would be caused by excessive interparticle agglomeration.

Still another object of the invention is to provide a powder-like recording pigment composed of essentially single-domain ferromagnetic cobalt or cobalt-containing particles of relatively uniform shape.

Another object of the invention is to provide a method of making cobalt and cobalt-containing particles having one or more of the above characteristics.

A further object of the invention is to provide superior magnetic recording members having the above improved ferromagnetic cobalt and cobalt-containing particles as the recording pigment.

Another object of the invention is to provide cobalt particles having sufficient alloying metal therein to markedly increase the oxidation resistance thereof, especially in the presence of moisture.

Other objects of the invention will be obvious to those skilled in the art on reading the instant application.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the particle possessing the feature, properties, and the relation of elements, which are exemplified in the following disclosure, and the scope of the invention will be indicated in the claims.

In general, the objects of this invention are accomplished by providing small, ferromagnetic cobalt and cobalt-containing particles of uniform shape which do not tend to agglomerate during their fabrication. These particles have a typical diameter of 0.02 to 0.5 micron and a typical length of 0.02 to 2.0 microns.

They may consist substantially entirely of cobalt or may contain cobalt alloyed with other metals. Nickel alloys have been found to be particularly advantageous. The actual particles which must ultimately be dispersed in a binder will be up to about 1 micron in length and will often be chain-like segments, i.e. acicular, consisting of more spherical elemental particles from about 0.01 micron to 0.2 micron in size, most advantageously from 0.02 to 0.07 micron.

Measurements on a bulk sample of unoriented cobalt-bearing particles of this invention give coercivities greater than 400 oersteds with typical values ranging from 600 to 1000 oersteds and more. The samples also have high saturation magnetization, in excess of 60

e.m.u./g. Still further, the bulk material is characterized by a high degree of squareness, e.g. ratios on the order of 0.25 to 0.6.

Thus we have found that the cobalt and cobalt-containing particles of this invention have magnetic and physical properties which make them especially suitable as the magnetic pigment in magnetic recording members. The advantages of the recording members are not only due to the magnetic characteristics of the particles noted above, but also they are due to the fact that particles can be oriented in essentially the same direction and can be distributed in a very thin layer with a close relationship to one another in a binder on a substrate. This, in turn, results in more uniform magnetic characteristics in a recording member incorporating these particles as the recording pigment.

Our process for producing magnetic particles may be divided into two basic parts. First, we create a multiplicity of very small, decomposable, acicular cobalt salt particles. Then, we coat the salt particles with, or immerse them in, an organic material such as silicone oil, polyacrylic ester resin, polyamide or the like, and heat the coated particles in a reducing atmosphere. The material minimizes inter-particle agglomeration or sintering so that each particle is reduced to a metal while still maintaining its individual acicular shape. The coating is substantially eliminated either by later washing in a suitable solvent or by thermal decomposition during the firing step, or by evaporation or sublimation or the like so that it does not materially degrade the magnetic and physical characteristics of a recording member incorporating the resulting metal particles.

Cobalt or cobalt-containing particles made in this way tend to be quite pyrophoric initially. Therefore, care must be taken at the outset to maintain them in a substantially oxygen-free atmosphere and to bring them into contact with oxygen relatively slowly. When this is done, a very thin oxide surface coating forms on the particles, retarding their further oxidation and thus rendering them stable. It should be understood that this oxide coating forms only a minor portion of each particle. Consequently, the particle is composed largely of pure cobalt or cobalt alloy.

The cobalt-containing crystals from which the cobalt particles are reduced are small and acicular. In accordance with the present invention, they are produced by a two-step, or successive, precipitation process. Specifically, we use a double precipitation process in which we first precipitate a compound having the requisite particle size but not the desired acicular shape. This first precipitate is then reacted to precipitate an acicular crystalline salt that can subsequently be treated to provide small metal particles.

The first precipitate is preferably highly insoluble and therefore it has a very low concentration in solution. The second precipitate is also highly insoluble. Consequently, there is little material in solution to support crystal growth of the second precipitate. As discussed below, this permits controlled acicular crystal growth and, specifically, it permits size control within desirable limits, e.g. about 0.01 to 2 microns in diameter.

More particularly, a finely-divided, cobalt-containing suspension such as the hydroxide or the carbonate is prepared by mixing an aqueous solution of sodium hydroxide or sodium carbonate with an aqueous solution of a cobalt salt, such as cobalt chloride. Then, oxalic acid is reacted with the suspension to form cobalt ox-

late. In practice, relatively low precipitation temperatures, e.g. 20°C, should be used because this tends to provide sufficiently small particle size. Also, each mixture is vigorously agitated to minimize agglomeration of the precipitated oxalate particles.

We do not fully understand why this process readily provides the desired oxalate particle size and shape. However, it appears that the parent hydroxide (or carbonate) particles serve not only as sources of the cobalt ions, but also as nucleating sites for the oxalate crystals. Secondly, with the very dilute solution resulting from low solubility, crystal growth is probably limited by a boundary layer around each crystal and, especially in a vigorously agitated suspension, the boundary layer is thinner at the ends than the sides of these particles, thereby promoting acicular growth. Furthermore, the parent particles serve as reservoirs to replace the cobalt ions that are taken up by the oxalate crystals.

In this fashion, the process provides the desired low concentration without requiring an unduly large volume of solution to provide a reasonably large yield of the organic cobalt salt. Also important is the fact that the hydroxide particles are used up in the process. These "disappearing" sites thus leave no impurities in the final material.

Moreover, the oxalate has a relatively low molecular weight; that is, the organic radical does not take up as much of the volume as would high molecular weight materials. In the ensuing reduction of the cobalt, this aids in providing compact particles with minimum shrinkage.

The precipitation is often carried out in a water-alcohol mixture or another such solubility-depressing medium to reduce the solubility of the precipitate to a level which discourages excessive growth of the oxalate crystals and facilitates particle shape and size control by means of the water-alcohol ratio. It also appears to facilitate control of the acicularity of the oxalate. Excellent results have been obtained with a 50 percent — 50 percent water-alcohol mixture and mixtures containing up to 90 percent alcohol have been tried with good results. In many circumstances, water alone is useful. Also, acetone and other water soluble solvents may be used in lieu of alcohol. Apparently for reasons not clearly understood some water is needed in order to produce reasonably good oxalate crystals.

In the case of cobalt oxalate, length-to-diameter ratios of the order of 10-to-1 have been obtained. On the other hand, with iron oxalate and iron-cobalt oxalate, length-to-diameter ratios are of the order of 3-to-1. These particles are further characterized by being very small, e.g. as low as 0.05 micron in diameter and by being relatively uniform in size. Cobalt content is preferably 43 percent of metal content in these cobalt salts.

During reduction of the oxalate crystals to metal particles, inter-particle agglomeration is preferably limited to maintain the particles below about 0.1 micron average diameter. In the most advantageous nickel:cobalt alloy particles the average diameter is maintained below about 0.05 micron.

It has been found that organic coatings and their residues keep the chain-type particles sufficiently apart during reduction to prevent excessive sintering at the high temperatures involved in hydrogen reduction. The coating can be such that the bulk of it is removed from the particle by decomposition during pyrolysis and subsequent heat treatment. Also it can be removed by sub-

sequent washing in a suitable solvent. In some cases it may evaporate or sublime. We intend that all of these processes be embraced within the term "removed." In any event, the coating does not unduly interfere with the physical and magnetic characteristics of the particle. The salt advantageously comprises a quantity of cobalt such that, on reduction of said salt to metal, the metal contains at least 43 percent cobalt.

Polymers and other organic chemicals that have been used as the coating material include silicone oil, silicone polymer, silanes, epoxy resin, polyacrylic ester, and polyurethane. Usually the organic material is applied in a suitable solvent to ensure complete coverage of the oxalate crystals. Alternatively, the particles can be immersed in the organic medium if it is a liquid such as, for example, a liquid hydrocarbon.

In selecting polymer coatings systems for use during reduction of a particular powder, it has been found helpful to subject the candidate polymer to a test comprising heating the polymer as it coats the metal particles at an elevated temperature, say 370°C., for 2 hours, in a nitrogen atmosphere. In general, those polymers that do not evaporate under test conditions and leave residues of above about 5 percent (based on the weight of the original polymer), have been found most useful. Most desirable are those polymers that will liquify during the reduction of the oxalate and before they reach their ultimate state of decomposition. Polyamides are particularly desirable for use with cobalt-bearing particles.

The range of organic material to be decomposed is conveniently from 1 to 15 percent by weight of the oxalate being reduced. Thus it is preferred that a very significant part of the polymer, preferably about 8 percent or more be left as residue. However, it is desirable that the major part of the residue be removed before use. In general, the decomposition residue should be less than 5 percent of the metal content of the oxalate.

Indeed, it is believed, but for the use of such coatings as described above, it would not be possible to achieve the high squareness values of the invention. Squareness values of 0.35 and above are achieved using these coatings during the sintering process, even using old-fashioned oxalate-preparation processes.

In the reduction step, the coated oxalate particles are heated to a temperature of approximately 325°-410°C in a reducing atmosphere such as hydrogen or hydrogen-nitrogen to reduce the cobalt (or cobalt alloy) and, at the same time, internally sinter the cobalt in each particle. If the reducing temperature falls much below 330°C, the oxalate crystals do not decompose readily. On the other hand, if the reducing temperature exceeds 400°C, excessive inter-particle sintering starts to occur and the resulting agglomerates degrade the magnetic characteristics of the material. We have found that a temperature of about 370°C produces optimum results.

Bulk samples of unoriented cobalt particles and cobalt-alloy particles of this invention exhibit particularly high coercivity and sigma values and are characterized by a high degree of squareness. In practice, masses of unbound particles exhibit coercivities ranging from 400 up to over 1,000 oersteds. The saturation magnetization values of our acicular cobalt powders range from 60 to 120 e.m.u./g. which is significantly greater than the corresponding values exhibited by conventional materials. Finally, our materials may have a squareness figure as high as 0.6. These attributes make the mate-

rial especially useful as the recording pigment in high-quality recording members.

The novel material produced by the present invention, and in particularly that material having squareness values over 0.35 and coercivities over 500, has a flat coercivity-to-temperature relationship compared to pre-existing ferromagnetic materials.

Coercivity values generally remain above 500 at 100°C and decrease only about 20 percent in magnetic coercivity between 0°C and 100°C. When such materials of the invention have been incorporated into polymer matrices as, for example, are used in fixing ferromagnetic materials to tapes for recording data, the resultant products show a surprisingly higher signal (unbiased sine-wave recording) output over a wider frequency than products heretofore known.

The magnetic measurements on the various samples in this application were done on a vibrating sample magnetometer at the Magnetic Laboratory at the Department of Electrical Engineering at the University of Minnesota. Generally, two hysteresis loops were traced for each sample: one at about 1 kilo-oersted peak-field at a field frequency of 60 Hz and one at about 8 kilo-oersted field. By measuring the saturation magnetic moment of the sample, one may calculate the fraction of pure cobalt in the sample as follows:

Fraction of cobalt = $4.7 / (1 + 582 / M_s)$ where M_s is the saturation magnetization of the sample in e.m.u./g.

Nickel is a particularly useful metal for use in forming cobalt alloys according to the process of the invention. It has been discovered that use of nickel allows one to more accurately pre-select the magnetic properties of the alloy. This may be because the nickel fits so well into a cobalt lattice system. In any event, the resultant nickel-cobalt alloys are predictably formed. Moreover, such alloys have outstanding resistance to degradation with time. That is, they have improved resistance to oxidation even under conditions of heat or humidity. Nickel alloys containing at least 43 percent, but preferably from 60 percent to 85 percent cobalt, are the most advantageous materials for use in many magnetic recording applications.

In order to point out more fully the nature of the present invention, the following specific examples are given as illustrative embodiments of the present process and products produced thereby.

EXAMPLE 1

A quantity of 238 g. of CoCl_2 is dissolved in a container to form a 1 liter aqueous solution. Then 100 g. of sodium hydroxide is dissolved in a second container to form a second 1 liter aqueous solution. The cobalt chloride and sodium hydroxide solutions are mixed together, using a magnetic agitator bar, in a 4 liter beaker for three minutes to form a cobalt hydroxide precipitate. Then 135 g. of oxalic acid are dissolved in a separate container to form a 1 1/2 liters aqueous solution. The oxalic acid solution is mixed thoroughly into the cobalt hydroxide precipitate for 5 minutes to form a cobalt oxalate precipitate. The resultant mixture is filtered in a Buchner funnel and washed several times with water. Then it is rinsed several times with acetone and air dried. The resulting cobalt oxalate particles are acicular, (that is "needle-shaped"). Following this, 0.05 g. of silicone polymer oil (sold under the trade designation, G.E. RTV910 Diluent) is mixed with 0.95 g. of the acicular cobalt oxalate particles using suffi-

cient tetrahydrofuran to insure uniform coating of the silicone oil on the particles. Next, the coated particles are air dried. Then the coated particles are charged into a 1 inch diameter glass tube in a tube furnace, heated to 360°C in a hydrogen atmosphere, and held at this temperature for 1 hour, thereby reducing the metal salt to cobalt. The material is then cooled to room temperature while still in a hydrogen atmosphere, and subjected to a 2 minute argon purge. Next the product is washed several times with acetone. A magnet is used to effect separation from the wash, and the separated material is air dried. The resulting product is a strongly magnetic powder having a coercivity of 705 oersteds, a sigma value of 82 e.m.u./g., and a squareness figure 0.40. The particles are composed mainly of cobalt, and have little or no silicone oil on their surfaces. Also the cobalt particles are acicular with an average particle size of 0.3 microns in diameter by 1 micron in length.

EXAMPLE 2

Cobalt particles are prepared as described in Example 1, except that the cobalt oxalate crystals are not coated with silicone oil during their reduction step. Now the resultant cobalt particles have a coercivity of 313 oersteds, a sigma value of 101 e.m.u./g., and a squareness characteristic of only 0.21.

EXAMPLE 3

Cobalt oxalate crystals are prepared in accordance with Example 1. Then 0.05 g. of silane, (sold under the trade designation Dow-Corning Z6020), is mixed with 0.95 g. of oxalate crystals prepared in accordance with Example 1 using a small quantity of tetrahydrofuran as a solvent for the silane to insure coating of the silane on the particles. Then the coated particles are air dried. Following this, the coated metal salt is charged into a glass tube in a tube furnace. The material is heated to 360°C under an argon atmosphere for ½ hour. It is held at 360°C under a hydrogen atmosphere for a period of 1 hour. Following this, it is cooled to room temperature while still in a hydrogen atmosphere and then subjected to a 2-minute argon purge. Then the cooled product is washed several times with acetone, using a magnet to affect separation of the particles after each wash, and air dried. The product obtained had a coercivity of 810 oersteds, a sigma value of 72.5 e.m.u./g. and a squareness characteristic of 0.43. The powder was composed of acicular cobalt particles.

EXAMPLE 4

A quantity of 2.0 grams of 2 1/2% epoxy-solution (5 g. of epoxy sold by Resyn Corporation under the name Resypox 1628, 0.75 g. of tetraethylenepentamine) in tetrahydrofuran is mixed with 0.95 g. of cobalt oxalate prepared in accordance with Example 1, and an additional quantity of 2.05 g. of tetrahydrofuran is added to insure complete coating of the oxalate particles. Then the coated material is air dried. The coated material is charged into a glass tube in a tube furnace, heated to 360°C in an argon atmosphere for ½ hour, and held at 360°C in a hydrogen atmosphere for 1 hour. Following this, it is cooled to room temperature while still in a hydrogen atmosphere and subjected to a 2-minute argon purge before being washed several times with acetone. A magnet is used to effect separation of the metal powder from the wash liquid. Thereupon the material is air dried. The dry product has a coercivity of 825 oersteds,

a sigma value of 75.5 e.m.u./g. and a squareness characteristic of 0.45. The powder is composed of essentially pure cobalt particles bearing little residual organic coating.

EXAMPLE 5

A quantity of 2.0 g. of 2 ½ percent G.E. SE-33 silicone gumstock dissolved in tetrahydrofuran is mixed with 0.95 g. of cobalt oxalate salt prepared in accordance with Example 1 and with 2.0 grams of tetrahydrofuran to insure complete coating of the salt particles. The coated material is then air dried (mixed). Following this the coated salt particles are charged into a glass tube, placed in a tube furnace, and heated to 360°C in an argon atmosphere for ½ hour. Then the material is held at this same temperature for 1 hour before being cooled to room temperature while still in the hydrogen atmosphere. Following a 2-minute argon purge, the material is washed with acetone using a magnet to effect separation from each wash liquid, and air dried. The product obtained is a ferromagnetic metallic powder having a coercivity of 750 oersteds, a sigma value of 77 e.m.u./g. and squareness characteristic of 0.42. The powder is composed of acicular cobalt particles.

EXAMPLE 6

A quantity of 238 g. of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ is dissolved in a container in 500 ml. of denatured alcohol and 500 ml. of water. Also 80 g. of sodium hydroxide is dissolved in a separate container in 500 ml. of water and 500 ml. of denatured alcohol. Then the solution is cooled to room temperature. Following this, the cobalt chloride and sodium hydroxide solutions are mixed together in a 4 liter beaker in a magnetic mixer for 5 minutes. During this period, a cobalt hydroxide precipitate forms in the beaker. In a separate beaker, 135 g. of oxalic acid are dissolved in 750 ml. denatured alcohol and 750 ml. of water. The oxalic acid solution is mixed into the cobalt hydroxide precipitate for 5 minutes to form a cobalt oxalate precipitate. The precipitate is filtered in a Buchner funnel and the oxalate cake is washed with 2 liters of acetone. Then the oxalate is redispersed in 1 liter of acetone and then filtered. The acetone-wet cake is mixed with 75 grams of 10 percent solution of Estane 5702, a polyurethane-type rubber, manufactured by B. F. Goodrich & Co. in tetrahydrofuran. This mix is spread on a polyethylene sheet to air dry. Coated oxalate salt is then charged into an aluminum boat which is approximately 16 inches long and 2 ½ inches wide and 1.9 inches high. The interior of this boat is separated into four elongate compartments by three equally spaced and centered fins. The filled boat is placed in a sealed 2 7/8 inch diameter stainless steel tube. The tube in turn is placed in a 3-inch diameter 24 inches long, tube furnace so that the filled aluminum boat is equally distant from each end of the furnace. Argon is fed through the stainless steel tube at a rate of 800 cc. per minute. At the same time, heat is applied to the stainless steel tube and in 1 hour the contents of the boat reaches 360°C. After 30 minutes, the atmosphere is changed to hydrogen, which is passed through the tube at a flow rate of 800 cc. per minute for a period of 2 hours. The stainless steel tube with the filled aluminum boat therein is taken out of the furnace and cooled externally with ice while still maintaining the boat in a hydrogen atmosphere and the contents allowed to reach

room temperature. Finally, a 10-minute argon purge is passed through the tube at a rate of 800 cc. per minute. The contents of the boat are then transferred to a polyethylene bag filled with argon. Care is taken to prevent contact with air, because at this point the material is extremely pyrophoric. After 4 days, two pinholes are pierced in the bag so that the contents of the bag are exposed to a very slowly increasing oxygen concentration. The product is then removed from the bag after 4 more days.

The resulting product obtained is ferromagnetic metallic powder having a coercivity of 813 oersteds, a sigma value of 86 e.m.u./g. and a squareness characteristic of 0.46. The powder is non-pyrophoric and is composed of acicular cobalt particles having cobalt oxide coatings and exhibiting minimal interparticle sintering.

EXAMPLE 7

A quantity of 100 g. of coated cobalt oxalate is prepared in accordance with Example 6 and charged into an aluminum boat. The boat is 16 inches long and 1.72 inches wide and 1.3 inches high and has two equally spaced lengthwise fins which divide the boat into three elongated compartments. The filled boat is charged into a sealed 2-inch diameter stainless steel tube. The tube is then placed in an aluminum muffle in a 3-inch diameter by 24-inch long tube furnace such that the filled aluminum boat is equally distant from each end of the furnace. Argon is then fed through the stainless steel tube at a rate of 400 cc. per minute. At the same time, heat is applied and the stainless steel tube is brought up to 380°C. Ninety minutes after startup, the gas is changed to hydrogen at a rate of 400 cc. per minute and temperature is maintained at 380°C for 120 minutes. Following this the stainless steel tube containing the filled aluminum boat is taken out of the furnace and cooled externally with ice and the contents allowed to reach room temperature in a hydrogen atmosphere. Then the reactor is purged with argon for 10 minutes at a rate of 400 cc. per minute. The contents in the boat are then transferred to a polyethylene bag with an argon atmosphere without allowing air to come into contact with the contents. After 4 days two holes are pierced in the bag so that the contents of the bag are exposed to oxygen only very gradually. After four more days the contents are removed from the bag. The product obtained is a ferromagnetic powder with a coercivity of 940 oersteds, a sigma value of 98 e.m.u./g. and a squareness characteristic of 0.45. The powder is composed of substantially acicular cobalt particles which carry oxide coatings so that they are stable.

EXAMPLE 8

Coated oxalate crystals are prepared in accordance with Example 6 except that the acetone wet cake is mixed with 75 g. of epoxy solution (10 grams of epoxy sold by Resyn Corporation under the name Resypox 1628, 1.4 grams of tetraethylenepentamine, 90 grams of acetone). The mix is spread on a sheet of polyethylene and air dried and allowed to cure at room temperature. Following this, a quantity of 100 g. of pre-coated cobalt oxalate is charged into an aluminum boat and reduced in accordance with the procedure described in Example 7. The material obtained is a black ferromagnetic powder having a coercivity of 938 oersteds, a sigma value of 113 e.m.u./g. and a squareness characteristic of 0.50. The powder is comprised of very small

acicular cobalt particles with oxide coatings which render them stable.

EXAMPLE 9

Cobalt oxalate crystals are prepared in accordance with Example 6 except that the acetone wet cobalt oxalate cake is divided into 22 forty-gram batches each batch containing 6.68 grams of cobalt oxalate. Each batch is then sealed in a 2-ounce bottle and is stored for use in subsequent work. Following this, 3.5 g. of an acetone solution containing 10 percent polyurethane sold under the trade designation Estane 5702 by B. F. Goodrich, is mixed with the contents of one bottle. The contents is then emptied from the bottle onto a polyethylene sheet, spread out and air dried. The mix is then charged into a 1-inch diameter glass tube in a tube furnace and heated to 360°C in an argon atmosphere for 20 minutes. The material is held at this temperature in argon for 25 minutes and held for a further 80 minutes at the same temperature in a hydrogen atmosphere. The mix is then cooled in the hydrogen atmosphere at room temperature and subjected to a 2-minute argon purge. The contents of the tube are then poured into an argon filled polyethylene bag and sealed. After 4 days, two holes are punched in the bag so that the oxygen gradually contacts the contents of the bag. The material removed from the bag is a ferromagnetic powder having a coercivity of 875 oersteds, a sigma value of 84 e.m.u./g. and a squareness characteristic of 0.415. The powder is composed of ferromagnetic acicular cobalt particles having oxide coatings which render them stable.

EXAMPLE 10

A quantity of 1.75 grams of an acetone solution containing 10 percent polyurethane sold under the trade designation Estane 5702 by B. F. Goodrich Co., are mixed with the contents of another bottle of the oxalate in Example 9 and the resulting mix is spread out on a sheet of polyethylene and air dried. This dried mix is charged into a tube and heated as described in Example 9. The resultant product is a ferromagnetic powder having a coercivity of 625 oersteds, a sigma value of 92 e.m.u./g. and a squareness characteristic of 0.31. Again the powder is composed of very small stable acicular cobalt particles.

EXAMPLE 11

A quantity of 7 grams of the polyurethane solution described in Examples 9 and 10 is mixed with the contents of a third bottle of oxalate stored for use in Example 9. The mix is then spread on a sheet of polyethylene and air dried. Following this the material is reduced as described in Example 9. The product obtained is a ferromagnetic powder having a coercivity of 937 oersteds, a sigma value of 79 e.m.u./g. and a squareness characteristic of 0.46.

EXAMPLE 12

The coated cobalt oxalate crystals are prepared in accordance with Example 9 except that the bottle contents are mixed with 3.5 grams of a 10 percent solution of Resypox 1574 solid epoxy sold by Resyn Corporation in acetone. The epoxy contains no curing agent. The resultant mix is spread on a sheet of polyethylene and air dried and reduced to produce a ferromagnetic powder as described in Example 9. The ferromagnetic

11

powder obtained has a coercivity of 875 oersteds, a sigma value of 92 e.m.u./g. and a squareness characteristic of 0.40.

EXAMPLE 13

A quantity of 3.5 grams of a solution containing 5 percent Estane 5702 polyurethane and 0.5 percent of a silica sold under the trade designation HiSil 233 in acetone is mixed with the contents of another bottle of the material in Example 9. The mix is then spread on a sheet of polyethylene and air dried. Following this it is reduced as described in Example 9. The powder obtained has a coercivity of 500 oersteds, a sigma value of 97 e.m.u./g. and a squareness characteristic of 0.30.

EXAMPLE 14

The material in another bottle of Example 9 is air dried and treated in accordance with that Example except that the cobalt oxalate salt particles are left uncoated. The product obtained is a powder composed of cobalt particles which are substantially sintered together. The material has a coercivity of 313 oersteds, a sigma value of 97 e.m.u./g. and a squareness characteristic of 0.22.

EXAMPLE 15

A quantity of 12.08 $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 10.0 g. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ is dissolved in 50 ml. denatured alcohol and 50 ml. of water in a container.

Also 8.0 g. sodium hydroxide is dissolved in 50 ml. alcohol and 50 ml. water in a second container. The two solutions are mixed together in a magnetic stirrer for 2 minutes at room temperature to form an iron-cobalt hydroxide precipitate. Then a quantity of 13.5 g. of oxalic acid dissolved in 75 ml. denatured alcohol and 75 ml. water is mixed with the precipitate for 2 minutes. The resultant mixture is filtered in a Buchner funnel and washed several times with acetone and air dried. Following this, 1.0 g. of the material is coated with a 5 percent Estane 5702 polyurethane described in Example 10 and charged into a 1 inch diameter glass tube in a tube furnace and heated for 30 minutes at 360°C in argon then it is held at 360°C in hydrogen for 90 minutes. Following this it is cooled to room temperature in hydrogen and then subjected to a 2 minutes argon purge. The resulting powder was composed of stable iron cobalt particles and had a coercivity of 750 oersteds, a sigma value of 90 e.m.u./g. and a squareness of 0.43.

EXAMPLE 16

A quantity of 10 g. of sodium hydroxide is dissolved in water to form a 100 ml. of solution. Also 23.8 grams of cobalt chloride $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ is dissolved separately in water to form a 100 ml. solution. The two aqueous solutions are then mixed together in a beaker in a magnetic mixer for 3 minutes forming a cobalt hydroxide precipitate. The precipitate is at room temperature. Then 150 ml. of 1 M oxalic acid is mixed into the cobalt hydroxide precipitate for 5 minutes at room temperature. The resultant product is a precipitate of cobalt oxalate salt which is then filtered in a Buchner funnel. Following this, the oxalate cake is washed several times with water, then with acetone, and finally is air dried. The resultant product is composed of cobalt oxalate crystals with an average particle size of 3.0 micron in length and 1.0 micron in diameter. Following this the

12

cobalt oxalate crystals are coated with 5 percent epoxy-hardener and reduced as described in Example 4. The resultant product is a ferromagnetic powder having a coercivity of 825 oersteds, a sigma value of 75.5 e.m.u./g. and a squareness characteristic of 0.45. The powder is composed of substantially unsintered acicular stable particles composed of cobalt. The particles have an average particle size of 0.3 micron in diameter and 1.0 micron in length.

EXAMPLE 17

A quantity of 238 g. sodium hydroxide is dissolved in a solution of 90 ml. denatured alcohol and 10 ml. water. Also 23.8 g. of cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) is dissolved in a second container with 90 ml. denatured alcohol and 10 ml. water. The contents of the two containers are mixed together in a magnetic mixer at room temperature for 5 minutes to form a cobalt hydroxide precipitate. Then 13.5 g. oxalic acid are dissolved in 135 ml. denatured alcohol and 15 ml. water are mixed with the cobalt hydroxide precipitate for 5 minutes at room temperature. The resultant mix is then filtered through a Buchner funnel, washed with acetone and air dried. The product obtained is a cobalt oxalate precipitate with the oxalate crystals having an average particle size of 0.1 micron in diameter and 1.0 micron in length. The cobalt oxalate crystals are then coated with a 10 percent epoxy solution-hardener and reduced as described in Example 8. The resultant product is a stable ferromagnetic powder composed of substantially unsintered cobalt metal particles having an average particle size of 0.035 micron in diameter and 0.35 micron in length. The powder has a coercivity of 750 oersteds, a sigma value of 29 e.m.u./g. and a squareness of 0.43.

EXAMPLE 18

The following three solutions are prepared.

A	20.0	grams methyl ethyl ketone
	0.10	gram of soya lecithin, Yelkins TTS
B	3.7	grams of Estane 5702 F1, B. F. Goodrich Chemical Company
C	10.0	grams of methyl ethyl ketone
	3.7	grams of Saran, F 130, Dow Chemical Company
	0.10	gram of Versilube F-50 silicone oil, General Electric Company
	12.0	grams of methyl ethyl ketone

A quantity of 17.0 grams of acicular cobalt powder is prepared as in Example 8. The cobalt powder is added to solution A while mixing in a Waring Industrial Blender and this mixture is allowed to stand for 17 hours. Solution B is then added slowly while mixing in the Waring Blender, and the resulting mixture is poured into a one quart steel jar containing 125 grams of $\frac{1}{4}$ inch diameter steel balls. The jar is capped and then shaken for 1.5 hours on a Red Devil Paint Conditioner, Model No. 5110. Then the mixture is separated from the steel balls by straining and weighing. For each 1.0 gram mix obtained, 0.47 gram of solution C was added under the action of the Waring Blender.

The resulting mix is then coated onto 1.42 mil polyethylene terephthalate film with a Bird Film Applicator and then passed over a 1,200 gauss bar magnet to achieve particle orientation. The film is dried for 5 minutes at room temperature and then 5 minutes at 100°C . The coated film is then subjected to measurements in

a Research Engineering and Development, Inc. B-H meter at 5,000 oersted applied field. The tape has a coercivity of 1,000 oersteds, a squareness characteristic of 0.6, and a saturation magnetization (Ms) of 2300 gauss. The volume fraction of cobalt in the coating in 21 percent. Conventional iron oxide tape prepared in the same way and with the same volume fraction of HR-280 iron oxide (by Hercules, Inc.) has a coercivity of 250 oersted, a squareness of 0.66 and an Ms value of 1,025 gauss.

EXAMPLE 19

A nickel-cobalt particle is formed using the procedure described below and the following quantities of reactants and solvents:

NaOH solution: 5 lbs., 13 oz. in 72 lbs, 10oz. of water.

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and CoCl_2 solution: 4 lbs., 8.5oz. of former salt and 10 lbs., 8.8oz. of latter salt in 66 lbs of water.

Oxalic acid solution: 10 lbs., 12 oz. of acid in 123 lbs. of H_2O .

Resymide 1125 solution: 100 grams

Alcohol added to Resymide solution: 600 grams.

An aqueous solution of COCl_2 is prepared. An aqueous solution of sodium hydroxide is poured into the cobalt chloride solution to form a precipitate of cobaltous hydroxide. A color change (to purple) is usually noted after the first 25 percent of the hydroxide solution has been added. After about two-thirds of the hydroxide solution is added, there is a thickening of the mix and care should be taken to avoid adding the hydroxide so fast that any portion of the thickening mix ceases to be well agitated during addition of the remainder of the hydroxide solution. Agitation is continued for a total of about seven minutes from the start of the hydroxide addition.

Thereupon an aqueous solution of oxalic acid is added to the cobaltous hydroxide slurry. This addition is carried out over about 90 seconds during which time the resulting slurry mixture of metal oxalate acquires a tannish-pink hue. After the addition, the slurry is mixed for about 8.5 more minutes before being filtered. The filtration is conveniently carried out in a pressure-filter having paper filter elements on four 18 inch diameter filter plates. The effective pore size of the paper is less than 1 micron.

It should be noted that the acicular metal oxalate subjected to filtration does not require the use of a filter aid; that is, the metal oxalate has what would be termed in the paper industry a high "freeness." It does not plug the filter and is sufficiently porous to facilitate a fast and effective separation of oxalate particles from the filtrate. It is thought that this characteristic is assignable to the acicular nature of the oxalate particles and a kind of bridging action which prevents a too-dense packing of the filter cake.

The resultant precipitate is washed twice with a mixture of 25 percent acetone in water. Thereupon, the precipitate is subjected to three more washings, each using acetone, and dried at about 30°C , i.e., at about ambient temperature.

The dried metal oxalate filter cake is placed in a $7\frac{1}{2}$ -gallon bowl of a food-type mixer. To this bowl is also charged an ethanol-based solution typically containing 100 grams of a commercially-available polyamide resin solution sold under the trade designation Resymid

1125 by Resyn Corp. After a mixing period of about 4 minutes, the resulting slurry is spread out on stainless steel pans and dried with circulating air at about 30°C . The dried material is passed with a Number 40 screen and loaded into seven aluminum reactor trays which are $2\frac{1}{2}$ feet by 1 foot by $\frac{1}{2}$ inch deep.

The trays are placed in a reactor so the oxalate contents do not contact the atmosphere within the oven. The reactor is closed and fitted with connections to accommodate the flow of purge gas, and purged with nitrogen for two hours. Then the purge gas is changed from nitrogen to a mixture of 10 percent hydrogen and 90 percent nitrogen and the heaters of the reactor are set at 722°F . The temperature rises to the 720°F - 725°F range over a period of about 3 hours. After this initial three-hour period, the material is heated within the 700° - 725°F for an additional 3 hours. During the third and fourth hours of this 6-hour period a considerable amount of CO_2 continues to be evolved from decomposing oxalate.

After a total heating period of from 6 - $6\frac{1}{2}$ hours, the oven door is opened and room temperature air is allowed to cool the reactor. The contents of the trays are still enclosed in the reactor and are under purge with the nitrogen/hydrogen mixture. After about 2 hours of such cooling, the reactor is taken out of the oven and cooled by being packed in ice for about 30 minutes, then equilibrated in ambient air for another 30 minutes.

The purge gas is now changed to a mixture of 3 percent oxygen and 97 percent nitrogen and this gas is used to slowly oxidize the surface of metal particles within the reactor for about 14 hours.

After the 14 hour period of controlled surface oxidation, the reactor is opened to the atmosphere, but the material is usually given another 3 to 5 hours to equilibrate with the atmosphere before being packaged and sealed in polyethylene bags.

The resultant material has the following magnetic properties:

Sigma value (σ)	87
Coercivity (H_c)	695
Squareness	0.50
H_w/H_c	3.5

In general, such nickel-cobalt particles with coercivity of over 500 and a squareness over about 0.4 seem to provide the most stable and desirable materials for use in magnetic recording applications.

Cobalt powders produced by the process of Example 19 have oil absorption values of from about 0.50 cc. of linseed oil per gram of powder to 2.00 cc per gram of powder. The variation is primarily caused by the nature and quantity of polymer residue thereon. Such materials also have a surprisingly low apparent bulk density of about 0.15 grams per cubic centimeter.

EXAMPLE 20

Although the most advantageous particles of the invention are prepared according to the use of oxalate particles formed according to the preferred double precipitation process, particles formed by other processes are also favorably influenced by use of a reduction procedure as used by this invention.

The process described in U.S. Pat. No. 3,574,685 to Haines is followed in making a small cobalt particle: A solution of 6 grams of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 75 milliliters of

dimethyl sulfoxide was mixed with a solution of 2.5 grams of oxalate acid in 75 milliliters of dimethyl sulfoxide. Thereupon 600 milliliters of water were added to the mixture and the resultant mix was agitated by shaking for 24 hours. Next, a precipitate of cobalt oxalate was recovered with a Buchner filter. The resulting filter cake was washed twice, each time with 100 ml. of water. Then the filter cake was washed three times more, each time with 50 ml. of acetone.

After this washed cobalt oxalate precipitate had been air dried, 1 gram of the cobalt oxalate material was charged into a glass tube and placed in a small furnace. The glass tube was equipped with appropriate connections to facilitate the transport of purge gas there-through.

The material was purged with hydrogen for 5 minutes then heated up to 335°C over a period of about 20 minutes under a hydrogen purge. After 335°C was reached, it was held for 3 hours, then cooked over a 50 minute period. The hydrogen purge was then discontinued and a nitrogen purge was used for 20 minutes. Thereupon, a mixture was passed over the product, now a metallic powder, for 3.5 hours.

The resulting cobalt powder was measured to have the following properties.

Sigma value (σ)	137 EMU per grams
Coercivity (H_c)	450 oersteds
Squareness	0.28
H_p/H_c	5.9

EXAMPLE 21

This example is presented to show the utility of resin coating during the high temperature reduction of cobalt powders manufactured by other than the optimum process.

A cobalt material was prepared according to the procedure of Example 20. A sample of the resultant powder was mixed with a polyamide resin solution. This solution was prepared from 40 grams of a material sold under the trade designation Resymide 1125 by Resyn Corporation and 320 grams of the denatured alcohol. The 0.5 gram of solution was diluted with another gram of alcohol before the cobalt powder was mixed therein. After mixing, the wetted powder was spread out at air dry at about 30°C.

About 0.9 gram of the dried material was placed in a small glass tube and charged to a furnace wherein it was treated under the following temperature — time — gas purge schedule.

Gas Purge	Time	Temperature during Time
Nitrogen	5 Minutes	Ambient
Hydrogen	20 Minutes	Ambient - 330°C
Hydrogen	3 Hours	330 - 360°C

Hydrogen	30 Minutes	Cooling
Hydrogen	20 Minutes	Cooling

After this the material treated with 3 percent oxygen and 97 percent nitrogen over a period of 3.5 hours at about 25°C.

The magnetic properties of the resultant powder were clearly improved over the properties of the powder of Example 20. The squareness was particularly improved.

Sigma value (σ)	137 EMU per gram
Coercivity (H_c)	525 oersteds
Squareness	0.37
H_p/H_c	4.3

It is of course to be understood that the foregoing examples are intended to be illustrative and that numerous changes can be made in the reactants, proportions, and conditions set forth therein without departing from the spirit of the invention as defined in the appended claims.

What is claimed is:

1. A dry powder-like composition consisting essentially of (1) acicular particles of metal oxalate crystals of at least an average 1.5:1 length-to-diameter ratio and (2) from 1 to 15 percent by weight of a polymeric resin intimately associated therewith, and forming a coating over said oxalate crystals.
2. A composition as defined in claim 1 wherein said organic material is solid thermally decomposable, polymeric resin which, on being heated to about 370°C in a non-oxidizing atmosphere will decompose, forming a liquid in the course of its decomposition.
3. A composition as defined in claim 1 wherein said organic material is a polyamide polymer.
4. A composition as defined in claim 1 wherein said oxalate contains nickel and iron as metal components thereof.
5. A dry powder-like composition formed of a mass (1) acicular particles of a metal-containing thermally decomposable organic salt crystals, and (2) a polymeric coating over said crystals.
6. A composition as defined in claim 5 wherein said salt contains a quantity of cobalt as a component thereof such that, on reduction of said salt to metal, said metal contains at least 43 percent cobalt.
7. A composition as defined in claim 5 wherein said metal comprises at least about 60 percent of cobalt and at least about 15 percent nickel.
8. A composition as defined in claim 5 wherein said polymeric coating liquefies in a reducing atmosphere below the decomposition temperature of said salt.
9. A composition as defined in claim 8 wherein said salt is an oxalate.

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