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## MAGNETIC MATERIALS AND METHODS OF MAKING THE SAME

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The invention relates to magnetic materials and to methods of making magnetic materials. More particularly, the invention relates to the preparation of ferromagnetic materials such as are used in the manufacture of magnetic recording members as for example magnetic tapes, ribbons, sheets, ink or the like.

The manufacture of magnetic materials for use as coatings on tape, ribbon, or the like or as pigments for printing magnetic surfaces is not new. Magnetic materials have been made by a variety of methods. However, the methods by which these materials have been made have been subject to a variety of problems and many attempts have been made to produce magnetic materials by methods which would not be subject to these problems and deficiencies.

It is well known in the art that various nonmagnetic oxides of iron can be converted to the magnetic form,  $\text{Fe}_3\text{O}_4$ , by the chemical process of reduction, e.g., by hydrogen gas at elevated temperatures, and that the  $\text{Fe}_3\text{O}_4$  can be further converted to  $\gamma\text{-Fe}_2\text{O}_3$ , an oxide with more desirable magnetic properties, by mild oxidation at elevated temperatures.

While the chemistry of such processes is simple, the technology is complex. Over-reduction and over-oxidation must be carefully avoided or deterioration of magnetic properties will result. Hazards in the use of a reducing gas at elevated temperatures are ever-present. The rapid currents of heated gases (both reducing and oxidizing) over and through agitated powders carry off fine particles.

The process of the present invention avoids the two-step operation of chemical reduction from a nonmagnetic iron oxide to  $\text{Fe}_3\text{O}_4$  and reoxidation to  $\gamma\text{-Fe}_2\text{O}_3$  which has characterized the practices of the prior art. It eliminates the danger of explosions and it eliminates the rather substantial material losses which occurred by reasons of these prior practices. In addition to eliminating these problems, the process of the present invention materially accelerates the steps of filtration, drying and conversion and has the additional advantage that it is self-sustaining and self-controlling in reaction. The finished product in the form of a magnetic material has magnetic properties which are equal to or better than the magnetic properties of prior art materials and has the additional advantage of improved dispersion properties in magnetic pigment formulations.

In the preferred practice of my invention, I suspend an oxide of iron in a solution of a soluble soap. I then add a solution of a salt which forms an insoluble compound with the salt. I next permit the insoluble material to precipitate, filter, wash and dry the solid and thereafter heat the reaction solids in air to a temperature sufficient to bring on an exothermic, self-promoting reaction which produces a magnetic material of superior dispersing properties and magnetic characteristics.

Broadly speaking, the procedure is to select a ferric oxide, preferably hydrated, of desirable size and shape and produced by any of the well-known precipitation techniques. This ferric oxide is slurried by agitation. The slurry may be the original formation liquor, or, if interfering ions are present, a washed or dewatered system derived from the original formulation. To this iron oxide slurry is added a soluble fatty acid soap, which results in a high degree of dispersion. A solution of a salt containing a cation capable of forming a highly insoluble compound with the anion of the fatty acid soap is slowly added to

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the slurry in stoichiometric proportions. The result is a curdy, readily filterable material. This product is filtered, washed, dried and powdered and thereafter heated entirely in air to a temperature of about  $100^\circ\text{C}$ . At about  $100^\circ\text{C}$ ., a spontaneous reaction sets in, which is self-promoting and controlling. When the reaction is complete, gas evolution ceases and the material cools down automatically. The final iron oxide pigment is a desirable end product for the formation of magnetic coatings. The following specific examples will more clearly point out the technique and process employed in this invention.

### Example I

103.1 pounds of a hydrated  $\alpha$ -ferric oxide, having a particle size in the range  $0.03\mu$  to  $0.4\mu$ , with an average acicularity of 4:1, were slurried in 49 gallons of water. To this was added a solution of 33.7 lbs. sodium oleate in 42 gallons of water and the two allowed to mix well. The dispersed slurry was agitated rapidly while a solution of 12.3 lbs. barium chloride dihydrate in 5 gallons of water was trickled in. Agitation was continued for 30 minutes and the slurry was then transferred to a filter. Rapid filtration ensued and the cake was washed to remove soluble salts. The filter cake was dried at  $60^\circ\text{--}70^\circ\text{C}$ . and passed through a #4 mesh sieve into a ventilated, rotating drum calciner. Mild heat was applied to the calciner until the exothermic reaction commenced. After three hours the reaction was complete and the material was cool enough to be removed. Mild pulverization yielded a magnetic powder with a coercivity of 270 oersteds and a remanence of 2000 gauss. A 20% formulation of the product in a soya modified, alkyd resin-toluene solvent coating formulation gave a low shear (10 r.p.m. Brookfield) viscosity of 80 centipoises. A like formulation with  $\gamma\text{-Fe}_2\text{O}_3$  possessed a viscosity of 92 cp.

### Example II

A sample of  $\alpha\text{-FeOOH}$ , grown from a conventional aqueous precipitation process, having particles in the size range  $0.2\mu$  to  $1.0\mu$  with an average acicularity of 10:1 was processed in accordance with the procedure in Example I. The final material had a coercivity of about 325 oersteds and a remanence of 2250 gauss. The resin formulation of Example I with this material yielded a viscosity of 72 cp.

### EXAMPLE III

A sample of  $\delta\text{-FeOOH}$  prepared by the process set forward in U.S. patent application Ser. No. 99,036, filed Mar. 29, 1961, and now Patent No. 3,115,470, having particles in the size range  $0.01\mu$  to  $0.2\mu$  and a laminar shape with an aspect ratio of about 3:1, was processed in accordance with the procedure set forth in Example I. The end product had a coercivity of 230 oersteds and a remanence of 1200 gauss. The resin formulation of Example I with this material yielded a viscosity of 64 cp.

### EXAMPLE IV

A sample of red  $\alpha\text{-Fe}_2\text{O}_3$  having particles in the size range  $0.03\mu$  to  $0.4\mu$  with an average acicularity of 4:1 were processed in accordance with the procedure in Example I. The final material had a coercivity of 300 oersteds and a remanence of 1650 gauss.

### EXAMPLE V

A series of materials were prepared in accordance with the procedure of Example I using  $\alpha\text{-FeOOH}$  having particles in the size range  $0.1\mu$  to  $1.0\mu$  and an acicularity of 4:1. Sodium soaps of various fatty acids and of constant mole ratio were used. Various salts, as chlorides or sulfates, were added on an equivalent mole ratio to the barium chloride in Example I (moles of insoluble soap constant). The magnetic properties of the final materials are listed in Tables I and II.

It has been found that the cation of the insoluble soap produced has an important effect on the final magnetic properties, while the anion effect is secondary. Barium fatty acid salts, for example, produce very good properties, as is shown in Table I by Preparations 1 through 4. Preparations 4a, 4b and 4c show the reproducibility from batch to batch. Preparations 4, 5 and 6 show that the quantity of precipitant present is not critical. Obviously, very small amounts would yield poorer results. Conversely, very large amounts could leave a large percentage of impurity in the product, which would "dilute" the remanence value proportionately. A 1:24 ratio yields a good product (compare with  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> tape pigment) and an adequate safety margin for processing.

The inequality of various cations in producing the desirable combination of magnetic properties is illustrated in Table II.

TABLE I

| Preparation | Precipitate                                                | Mole Ratio<br>ppt. to<br>Fe <sub>2</sub> O <sub>3</sub> | Coercivity<br>(oersteds) | Remanence<br>(gauss) |
|-------------|------------------------------------------------------------|---------------------------------------------------------|--------------------------|----------------------|
| 1.....      | Barium Stearate.....                                       | 1:24                                                    | 230                      | 2,050                |
| 2.....      | Barium Palmitate.....                                      | 1:24                                                    | 280                      | 2,000                |
| 3.....      | Barium Linoleate.....                                      | 1:24                                                    | 250                      | 1,900                |
| 4a.....     | Barium Oleate.....                                         | 1:24                                                    | 280                      | 2,250                |
| 4b.....     | do.....                                                    | 1:24                                                    | 270                      | 2,000                |
| 4c.....     | do.....                                                    | 1:24                                                    | 260                      | 1,950                |
| 5.....      | do.....                                                    | 1:18                                                    | 280                      | 2,200                |
| 6.....      | do.....                                                    | 1:34                                                    | 280                      | 2,400                |
|             | $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> Tape Pigment..... |                                                         | 270                      | 2,100                |

TABLE II

| Preparation | Precipitate                  | Mole<br>Ratio | Coercivity<br>(oersteds) | Remanence<br>(gauss) |
|-------------|------------------------------|---------------|--------------------------|----------------------|
| 7.....      | Aluminum Hydroxy Oleate..... | 1:24          | 340                      | 1,200                |
| 8.....      | Calcium Oleate.....          | 1:24          | 260                      | 2,450                |
| 9.....      | Cobalt Oleate.....           | 1:24          | 350                      | 1,300                |
| 10.....     | Copper Oleate.....           | 1:24          | (350)                    | 600                  |
| 11.....     | Hydrogen Oleate.....         | 1:12          | 290                      | 1,450                |
| 12.....     | Iron Oleate.....             | 1:24          | (300)                    | (200)                |
| 13.....     | Lead Oleate.....             | 1:24          | 190                      | 1,950                |
| 14.....     | Magnesium Oleate.....        | 1:24          | 240                      | 1,150                |
| 15.....     | Manganese Oleate.....        | 1:24          | (350)                    | 700                  |
| 16.....     | Nickel Oleate.....           | 1:24          | 300                      | 1,200                |
| 17.....     | Strontium Oleate.....        | 1:24          | 200                      | 2,100                |
| 18.....     | Zinc Oleate.....             | 1:24          | 320                      | 1,300                |

( ) Data approximated from extrapolation of instrument readings.

It is clear from the foregoing tables that the highest values of remanence and coercivity are attained when using a cation from the alkaline earth group calcium, barium, and strontium although other metals produce satisfactory materials as may be seen from the tables.

While I have illustrated and described certain preferred practices and products in the foregoing specification, it will be understood that this invention may be otherwise practiced within the scope of the following claims.

I claim:

1. A process for producing a magnetic pigment of superior dispersing properties and magnetic characteristics comprising the steps of suspending a nonmagnetic oxide of iron in aqueous slurry, adding to the slurry a solution of a soluble soap, adding to the slurry containing the soap a soluble salt of an alkaline earth metal to form an insoluble soap, precipitating the insoluble soap formed by the addition of the alkaline earth metal salt, filtering, drying and heating to a temperature sufficient to initiate a gas evolving reaction in the mass, permitting the reaction to continue until completion in air and recovering the reacted precipitant as a magnetic pigment.

2. A process as claimed in claim 1 wherein the mass is heated to about 100° C. to initiate reaction.

3. A process for producing a magnetic pigment of superior dispersing properties and magnetic characteristics comprising the steps of suspending a nonmagnetic

oxide of iron in aqueous slurry, adding to the slurry a solution of a soluble soap, adding to the slurry containing the soap a salt of barium, precipitating the insoluble soap formed by the addition of the barium salt, filtering, drying and heating to a temperature of about 100° C. to induce a gas evolving reaction, permitting the reaction to continue until completion in air and recovering the reacted precipitant as a magnetic pigment.

4. A process for producing a magnetic pigment of superior dispersing properties and magnetic characteristics comprising the steps of suspending a nonmagnetic oxide of iron in aqueous slurry, adding to the slurry a solution of a soluble soap, adding to the slurry containing the soap a soluble salt of calcium, precipitating the insoluble soap formed by the addition of the calcium salt, filtering, drying and heating to a temperature of about 100° C. to induce a gas evolving reaction, permitting

the reaction to continue until completion in air and recovering the reacted precipitant as a magnetic pigment.

5. A process for producing magnetic pigment of superior dispersing properties and magnetic characteristics comprising the steps of suspending a nonmagnetic oxide of iron in aqueous slurry, adding to the slurry a solution of a soluble soap, adding to the slurry containing the soap a soluble salt of strontium, precipitating the insoluble soap formed by the addition of the strontium salt, filtering, drying and heating to a temperature of about 100° C. to induce a gas evolving reaction, permitting the reaction to continue until completion in air and recovering the reacted precipitant as a magnetic pigment.

#### References Cited

##### UNITED STATES PATENTS

|           |         |                     |          |
|-----------|---------|---------------------|----------|
| 3,047,429 | 7/1962  | Stoller et al. .... | 252—62.5 |
| 3,278,440 | 10/1966 | Schuele .....       | 252—62.5 |
| 1,843,862 | 2/1932  | Buc .....           | 23—1     |
| 2,623,849 | 12/1952 | Peterson .....      | 23—200   |
| 2,689,167 | 9/1954  | Dovey et al. ....   | 23—200   |
| 3,084,123 | 4/1963  | Hund .....          | 252—62.5 |

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