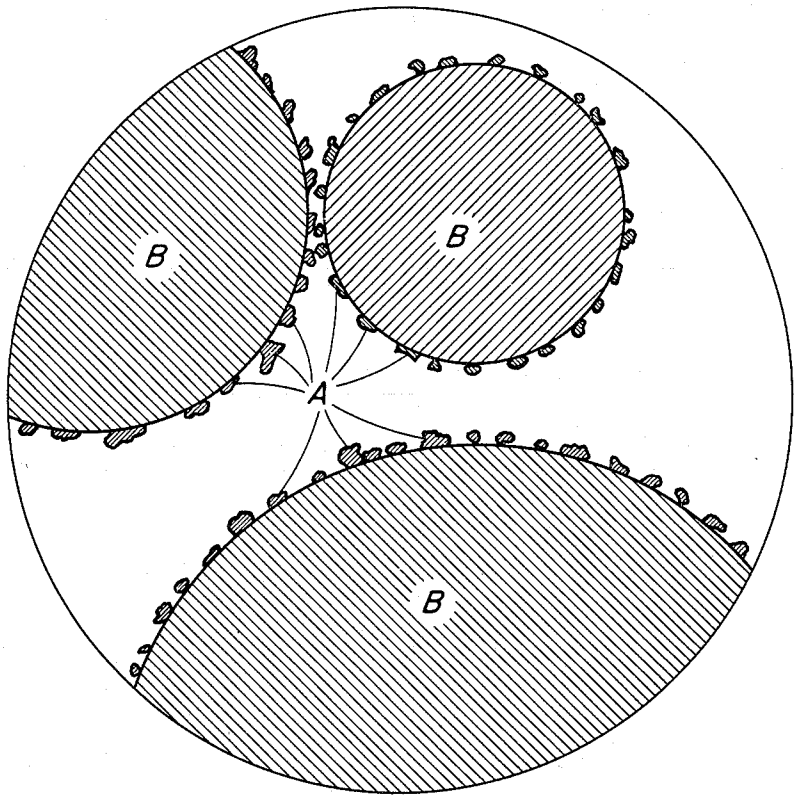
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PROCESS OF PREPARING IRON POWDER OF IMPROVED ELECTROMAGNETIC AND MECHANICAL PROPERTIES

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PROCESS OF PREPARING IRON POWDER OF IMPROVED ELECTROMAGNETIC AND MECHANICAL PROPERTIES

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The present invention relates to an iron powder of improved electromagnetic and mechanical properties and to the process of preparing the same.

Iron powder obtained by the thermal decomposition of iron pentacarbonyl is usually in the form of microscopic spheres each of which is composed of several hundred submicroscopic crystals. These contain 1 to 2% of impurities, i. e., approximately 0.2% of oxygen, 0.7% of carbon, and 0.5% of nitrogen. The powder is prepared by introducing the iron carbonyl into a heated vessel in such a manner that the decomposition takes place substantially in the free space of the vessel instead of by contact with the heated walls of the vessel as described in United States Patent 1,759,659. When such a powder is processed into a magnetic core, the smallness of the crystals and the relatively large amount of impurities seriously limit compressibility and density. It is impossible to obtain bodies with densities higher than 5.2 grams per cubic centimeter or with more than 70% of their volumes covered by iron. This restricts magnetic initial permeability to values of less than 20.

In order to obviate the foregoing defect, it has been proposed that the powder be subjected to a heat treatment in a reducing atmosphere as described in United States Patent 2,508,705. This step increases crystal size and removes most of the impurities. Consequently, permeabilities of 70 and even above become possible. Powders which yield high permeabilities are highly desirable as material for magnetic cores of high frequency coils. The higher permeability provides a wider range of inductance variation or frequency coverage or effective heights for various coils, while at the same time requiring less turns of wire and thus increasing the Q values. The latter must be maintained high also by the small particle sizes and consequent low eddy current losses as well as by low residual losses.

Some of the drawbacks of the method described in the latter patent are the unavoidable sintering and cluster formation of a large proportion of particles during the reduction treatment. This entails a great deal of machine and hand labor in order to recomminute the powder to the required size. Particularly, the discharge of the sintered cakes from the trays or pans is laborious and difficult. Powerful and expensive crushing and pulverizing machinery, whose maintenance presents serious problems, has to be used. Very often extensive ball milling is necessary which requires frequent cleaning and overhauling of the mill. One powder grade can only be obtained by the use of thinner layers in the furnace (only 40% as thick as the others) thus reducing yields per unit time and increasing cost. The resulting powders contain many particle agglomerations or clusters in spite of the comminution treatment, thus keeping eddy current losses high and Q values low. Moreover, a great many particles are deformed or have work-hardened surfaces or both. This detracts appreciably from compressibilities, permeabilities, and Q values that the powders could theoretically attain.

The meaning of the term "Q value" as used herein may be defined as follows:

$$Q=\frac{\text{Reactance of coil}}{\text{Series resistance}}=\frac{2\pi FL}{R}$$

L=Coil inductance (henries)

R=Series coil resistance (ohms)

F=Frequency at which L and R are measured

As can be seen from the above formula, the value of "Q" will generally increase with an increase of coil inductance and decrease with an increase in coil resistance. The addition of an iron core will increase the inductance but also introduce eddy current and other losses. These losses act as and can be represented as an increase in effective coil resistance.

I have now found that the properties and performance of iron powders are substantially improved by the use of a new production process. This process avoids all of the above drawbacks, is simpler and hence less expensive, and yields a powder of such superior properties that the hitherto unavoidable step of insulation in high frequency core fabrication may be entirely omitted.

The process yields ferromagnetic powders having an initial magnetic permeability above 100 at 100 tons/in.^{2} molding pressure, eddy current loss coefficients below 0.1×10^{-6} ohms per henry and cycles-per-second-squared at not more than 60 tons/in.^{2} molding pressure without any insulation treatment of the powder after reduction, and residual losses at any molding pressure below 15×10^{-3} ohms per henry and cycles-per-second.

To provide a process which yields ferromagnetic powder having the foregoing properties constitutes the object of the present invention.

Other objects and advantages will appear from the following description.

The ferromagnetic powder having the foregoing properties is prepared from any non-reduced carbonyl iron powder by first subjecting the iron powder to a treatment in which fine particles of an insulating material are attached to the surface of the spherical iron powder particles.

The particles of the insulating material must be considerably smaller in size than the iron powder particles, so as not to take up appreciable space in the core and in this way reduce the overall magnetization or field strengths produced by magnetizing fields emanating from coils, etc. It was found that a convenient particle size of the insulating material is one having a diameter of a few hundredths of a micron. The insulating particles are approximately $\frac{1}{100}$ in diameter of the diameter of the carbonyl iron particles.

The insulating materials or refractory powder, of which these small particles are fashioned may be any material which is refractory in a reducing atmosphere up to 700° C. For this purpose, I have found that metallic silicates are especially suited. Any metallic silicate, including the alkali and alkaline earth silicates, such as sodium, potassium, lithium, etc., having particle sizes of the foregoing magnitude may be employed. For reasons of commercial availability, cheapness of price, and better results, I prefer, however, to employ aluminum, barium, calcium, copper, nickel, magnesium, manganese, zinc, strontium, and ferrous silicates.

The main feature of the process is the attachment of these insulating particles to the surface of the carbonyl iron particles. It is not sufficient to merely mix the two components. It is necessary to use force or pressure. The force or pressure can be conveniently supplied by

balls in a rotating mill. In order to achieve the desired degree of dispersion of the small particles and to press them unto the surface of the carbonyl iron particles with sufficient energy to assure their adherence during manipulation and reduction treatment, it is necessary to mill for a certain minimum time and with a certain minimum of milling bodies. On the other hand, too much milling may shatter the carbonyl iron particles and thus produce iron particles of lessened usefulness because they have become either too small or too irregularly shaped. Practical limits thus are ratios of milling bodies to milling charge of 1:1 to 6:1 (by weight) and milling times of 1 to 10 hours, the latter depending upon the former so that more time is required for low ratios and vice versa. Size and speed of the mill are also of importance and will influence the choice of milling ratio and time. In general, the speed recommended by the manufacturer of the mill is used. This speed is half of the so-called "critical speed" which is defined as being of a magnitude where the centrifugal forces that develop inside the mill reach values which cause the relative motion between the mill and its contents to approach zero. Furthermore, it is advantageous to exclude oxygen or any other gases which may react with the powders in the ball mill.

During the milling operation any gaseous mixture, provided it consists essentially of nitrogen ranging from 75–85%, may be employed. In this mixture the presence of carbon dioxide, carbon monoxide, helium, hydrogen, and the like is not detrimental so long as the mixture is free from oxygen. Instead of a gaseous nitrogeneous mixture, the gas may be pure nitrogen or nitrogen containing impurities other than oxygen in large amounts. In other words, the oxygen content should be below 1%. For practical purposes, I have found that a gaseous mixture consisting of 80–85% nitrogen and 15–20% of carbon dioxide and 1% of gases other than oxygen give satisfactory results. Pure nitrogen likewise gives excellent results but is more costly than the mixture.

The proportion of refractory powder to carbonyl iron powder has to be below 1%, i. e., in the range of 0.1 to 0.5%, preferably about 0.2%. The amount needed can also be derived by simple computation. For example, iron powder whose surface-average diameter is 6 microns has a surface of 1,280 cm.^{2} per gram. In order to cover one fourth of this surface by silicate particles of an average diameter of 0.03 micron and a density of 2.9 g./cm.^{3}, an amount of 0.00186 gram of silicate per gram of iron or approximately 0.2% are required.

The next step of the process is the heat treatment in a reducing atmosphere. Preferably, hydrogen with no more than a few tenths of a per cent of impurities, such as oxygen, water vapor, and occasionally small amounts of nitrogen, at temperatures between 450–650° C., treating times-on-temperature between 5 to 20 hours and a flow rate of hydrogen to give a total of hydrogen of from 3 to 6% by weight of the weight of the powder charge are used. This is a conventional reduction treatment which yields iron powder containing less than 0.1% carbon, 0.3% oxygen, and 0.1% nitrogen, with all other elements present in traces only.

The resulting powder will pass through a sieve of 200 meshes per linear inch without difficulty and without the necessity of further milling or of other comminution methods. It is an essential part of this invention and an entirely new feature that this powder has retained its pulverulence in spite of the severe heat treatment which would cause a similar powder not processed as described above to sinter strongly and to form large and tough sinter blocks which require the expensive comminution equipment and maintenance mentioned above.

It is furthermore an essential feature of this invention that the process yields a powder whose particles by virtue of carrying a large number of small electrically non-conductive particles on their surfaces very rarely contact each other even after compression and thus behave as though insulated by conventional means. Hence, it is not necessary, though possible if desired, to subject the powder to the usual step of particle insulation which is the first step taken in fashioning magnetic cores from iron powders. This represents a further considerable saving.

The establishment of the adherence of small refractory insulating particles to the surface of the carbonyl iron particles has been determined not only indirectly by electromagnetic measurements but also directly by electron-microscopic photographs. The single figure constituting the accompanying drawing illustrates the adherence of such particles to each other. By reference to the drawing, wherein A represents the refractory insulating material and B the carbonyl iron particles, it will be noted that the insulating particles adhere to the surfaces of the carbonyl iron particles. The illustration of the drawing is reproduced as a portion of a photograph obtained by the electron microscope.

In addition to the property of being insulated, the powder possesses remarkable characteristics which distinguish it from all other carbonyl iron powders and from all other metal powders. It combines with small particle size an advantageously high compressibility and magnetic permeability.

A fairly complete recent survey of magnetic materials by Richards et al. in "Proceedings of the Institution of Electrical Engineers," part II, vol. 97, pages 236–245, April 1950, lists as the highest permeability obtainable (with reasonable eddy current and residual loss coefficient, i. e., below 0.1×10^{-6} and 15×10^{-3}, respectively, and a pressure of 50 tons/in.^{2}), the value of 30, with carbonyl iron type L. The new powder prepared in accordance with the present invention will give permeabilities at least 5% higher than those of type L, while having much more favorable loss coefficients. In another paper by G. O. Altmann and H. Beller in "Electronic Industries," November 1945, page 86, an improved type of carbonyl iron powder is described with permeabilities of 55 to 70 and possibly 77. The new powder also yields a permeability of above 100 at the molding pressure of 100 tons/in.^{2}.

The following examples will describe in detail the methods for accomplishing the above objects, but it is to be understood that they are inserted merely for the purpose of illustration and are not to be construed as limiting the scope of the invention.

Example 1

100 lbs. of iron powder obtained by decomposition of iron pentacarbonyl at between 250–300° C. and having a weight-average particle diameter of about 8 microns was placed in a ball mill of 90 gallon capacity together with 200 lbs. of steel balls, 5/8 inch in diameter, and with 0.2 lb. of a calcium silicate powder of 0.03 micron diameter. The mill was rotated at 28 R. P. M. for 3 hours. A gas mixture composed of approximately 83% nitrogen, 16% carbon dioxide, and 1% of various other gases was maintained inside the mill.

The powder was then placed in a steel boat and treated in an atmosphere of hydrogen for 9 hours at 550° C. while a flow of 0.5 C. F. M. of hydrogen was maintained throughout. After discharge, the powder passed easily through a 200-mesh sieve without leaving a coarse residue above the sieve.

A portion of this powder was then worked into high frequency cores in the following manner:

50 grams of the powder were thoroughly mixed with a phenolic binder by applying 0.5 gram of furfural formaldehyde resin in acetone and evaporating the solvent. A grainy powder results which was further mixed with 0.1 gram of a waxy lubricating powder, sold under the brand-name of Acrawax-Atomized C (available from the Glyco Products Company). 6.5 gram lots of this powder were molded into rectangular bar-shaped cores of about 0.2

inch square cross-section and 1.5 inch length, using a pressure of 50 tons per square inch. The cores were cured for 30 minutes at 170° C. to harden the binder and then given a surface phosphatizing treatment to remove scale and prevent rusting. The cores were then subjected to electromagnetic tests, described below, which showed the following values:

(a)	Permeability at 100 tons/in.² molding pressure.	108.
(b)	Eddy current loss coefficient at 50 tons/in.² (no insulation treatment.	0.08×10^{-6} ohms per henry and cycles-per-second-squared.
(c)	Residual loss coefficient	10.5×10^{-3} ohms per henry and cycles-per-second.

Control tests omitting the step of milling with refractory powder resulted in excessively sintered powder which could be broken up only with difficulty and then had about 20% of its particles of a size that would not pass through a 200-mesh sieve and the fraction that did pass through the 200-mesh sieve showed eddy current losses of about 0.5×10^{-6} ohms per henry and per cycles-per-second-squared (or six times the above value) after being worked up into cores in a manner identical to the above described procedure.

The electromagnetic tests are performed with Q meters from which Q values and tuning capacitances are read directly. From these values permeabilities and loss coefficients are readily obtained.

The standard method and the calculations employed in determining "initial permeability" and "eddy current loss coefficient" are modifications of the method described in an article by V. Legg, entitled "Magnetic Measurements at Low Flux Densities Using the A. C. Bridge," in Bell System Technical Journal, vol. 15 (1936), page 39. The method involved uses the measurement of the apparent Q value (quality factor) of the core, by means of a Q-meter while the core is inserted in a solenoid energized by various A. C. frequencies (f) up to 10 megacycles. The apparent Q values, determined by direct measurement, were corrected in accordance with the characteristics of the measuring instrument to yield actual Q values.

To determine initial permeability at 100 tons per square inch molding pressure, toroids were made of the powder directly and wound with sufficient turns to yield an inductance (L) of 1.0 millihenry. The initial permeability (μ) was calculated from the inductance (L) at 1 kilocycle, extrapolated to zero current, and from the calculated effective magnetic diameter of the core.

The eddy current and the residual loss coefficient were determined from the loss resistance up to 10 megacycles.

The effective resistance of the core (R_{eff}) is calculated from the Q value, frequency (f), and inductance (L) in accordance with the formula:

$$R_{eff}=2\pi fL/Q$$

The effective resistance (R_{eff}) is the sum of the D. C. resistance (R_0) and the high frequency loss resistance components, respectively, due to the eddy current loss, residual loss, and other losses. This relationship is expressed by the equation:

$$R_{eff}=R_0+cLf+eLf^2+kL^2f^3$$

wherein the second term of the sum represents the residual loss resistance, c being the residual loss coefficient; the third term represents the eddy current loss resistance, e being the eddy current loss coefficient, and the last term being the dielectric leakance loss with a coefficient k which, however, is of no importance in these examples. All of the terms can be calculated from the measurements indicated above. The eddy current loss coefficient is then obtained in units of ohms per henry and cycles-per-second-squared, while the residual loss coefficient is obtained in units of ohms per henry and cycles-per-second.

Example 2

200 lbs. of iron powder obtained by decomposition of iron pentacarbonyl and having a weight average diameter of 5 microns were placed in a 90 gallon capacity ball mill together with 200 lbs. of 1.5 inch diameter steel balls and with 0.6 lb. of colloidal clay, a hydrous silicate of alumina. The mill was run for 6 hours at 28 R. P. M. in a nitrogen atmosphere.

The heat treatment consisted of 8 hours at 650° C. in an atmosphere of hydrogen, flowing at a rate of 1 C. F. M. The powder was screened through a 200-mesh sieve. No coarse particles were retained by the sieve. The powder was worked up into high frequency cores in a manner identical to the one described in the above example. The corresponding electromagnetic values obtained were as follows:

(a)	Permeability at 100 tons/in.² molding pressure	105.
(b)	Eddy current loss coefficient at 50 tons/in.² (no insulation treatment)	0.075×10^{-6} ohms per henry and cycles-per-second-squared.
(c)	Residual loss coefficient	10×10^{-3} ohms per henry and cycles-per-second.

Example 3

500 grams of iron powder obtained by decomposition of iron pentacarbonyl and having a weight-average diameter of 8 microns were placed in a 1-quart ribbed steel mill together with 1000 grams of ¾ inch balls and with 1 gram of ferrous silicate. The mill was run for 4 hours at 100 R. P. M. after being first purged with nitrogen and then sealed.

The heat treatment was carried out in a muffle furnace, holding 100 grams of the milled powder in an atmosphere of hydrogen, flowing at 4 liters/min. for 16 hours at a temperature of 500° C. The powder easily passed a 200-mesh sieve upon cooling and removal from the furnace.

Its permeability and loss factors, when worked up into cores, were the same as those cited in Example 1 within limits of ± 3%.

Example 4

For comparison purposes, corresponding values of commercial, reduced carbonyl iron powders were determined and are listed in table form below. These were made by starting with the same crude powder, but no surface film is applied prior to reduction. The sintering that develops during the reduction heat treatment requires special comminution methods as well as, later on, surface insulating coating as the first step of fabrication into high frequency cores.

Temperature of reduction (° C.)	410	410	460	460
Insulation	None	Mild	None	Mild
(a) Permeability at 100 tons/in.² molding pressure	90	80	82	65
(b) Eddy current loss coefficient at 50 tons/in.² ($\times10^{-6}$ ohms per henry and cycles-per-second-squared.)	0.25	0.07	1.0	0.16
(c) Residual loss coefficient ($\times10^{-3}$ ohms per henry and cycles-per-second.)	11	11	19	19

The foregoing data clearly demonstrate the advantages of the present process as heretofore described.

While I have disclosed the preferred embodiments of my invention and the preferred modes of carrying the same into effect, it will be readily apparent to those skilled in this art that many variations may be made therein without departing from the spirit thereof. Accordingly, the scope of my invention is to be limited only by the following claims.

I claim:

1. The process of improving the electromagnetic properties of carbonyl iron powders while obviating the steps

of comminution and insulation which comprises subjecting pulverulent iron obtained by decomposition of iron pentacarbonyl to a milling treatement in the presence of a metallic silicate to induce the attachment of refractory particles to the surface of the iron powder particles, and subsequently reducing the treated powder with hydrogen at temperatures ranging from 450 to 650° C.

2. The process of improving the electromagnetic properties of carbonyl iron powders which comprises subjecting pulverulent iron obtained by thermal decomposition of pentacarbonyl iron to a milling treatment in a gaseous atmosphere consisting essentially of nitrogen and in the presence of a metallic silicate, and reducing the treated powder with hydrogen at a temperature ranging between 450 to 650° C.

3. The process of improving the electromagnetic properties of carbonyl iron powders which comprises subjecting pulverulent iron obtained by thermal decomposition of pentacarbonyl iron to a milling treatment in a ball mill running at approximately one-half critical speed, with ratios of milling bodies to iron powder of from 1 to 1 and 6 to 1, in the presence of a metallic silicate and a gaseous atmosphere consisting essentially of nitrogen, for a period of time ranging from 1 to 10 hours, and reducing the treated powder with hydrogen at a temperature ranging between 450 to 650° C.

4. The process of improving the electromagnetic properties of carbonyl iron powders which comprises subjecting pulverulent iron obtained by thermal decomposition of pentacarbonyl iron to a milling treatment in a ball mill running at approximately one-half critical speed, with ratios of milling bodies to iron powder of from 1 to 1 and 6 to 1, in the presence of a metallic silicate in the proportion of 0.1 to 0.5% based on the weight of the carbonyl iron powder, and a gaseous atmosphere consisting essentially of nitrogen, for a period of time ranging from 1 to 10 hours, and reducing the treated powder with hydrogen at a temperature ranging between 450 to 650° C.

5. The process according to claim 2, wherein the metallic silicate is calcium silicate.

6. The process according to claim 2, wherein the metallic silicate is aluminum silicate.

7. The process according to claim 2, wherein the metallic silicate is ferrous silicate.

8. The proces according to claim 2, wherein the metallic silicate is barium silicate.

9. The process according to claim 2, wherein the metallic silicate is copper silicate.

References Cited in the file of this patent

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