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2,744,040

PROCESS OF PREPARING IRON POWDER FOR MAGNETIC CORES

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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.

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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 non-reduced, carbonyl iron powders having a carbon content ranging from 0.1 to 1.2% by a surface treatment in order to give its particles a protective surface layer followed by the usual reduction treatment. The first step of the process, the coating of the carbonyl iron powder, is carried out by mixing the carbonyl iron powder in any mechanically or electrically agitated vessel with 0.1 to 0.5% by weight of the iron powder of a silicone resin. The silicone resin or silicone polymers, employed in accordance with the present invention, are prepared by the acid base or water polymerization of monomeric organic derivatives of orthosilicic acid in which one or more hydroxyl groups is replaced by an alkyl group, e. g., methyl, ethyl, propyl, butyl, and the like, or an aryl group, such as phenyl. The preparation of such thermosetting organo-silicone resins is well known and need not be described herein. As examples of such resins, the following may be mentioned:

Methyl silicone resin
Ethyl silicone resin
Phenyl methyl silicone resin.

In addition to the foregoing specific silicone resins, organo-silicone compounds in which a plurality of divalent organic radicals are each linked to two separate (different) silicone atoms, as described in United States Patent 2,383,817, may be employed. Poly lower alkyl-dichlorosiloxanes prepared according to the method described in United States Patent 2,381,366, the polymerized monomethyl, monoethyl, monopropyl, and monophenyl resins prepared according to the method described in United States Patent 2,375,998, and the resins obtained by the acid base, or water polymerization of dimethyl, diethyl, dipropyl, and dibutyl dichlorosilanes and

trimethyl, triethyl, tripropyl, and tributyl chlorosilane may also be employed, including the polymers of methyl silicone triol and phenyl silicone triol prepared according to United States Patent 2,375,998.

The polymeric silicones are preferably employed in the form of a solution in a hydrocarbon solvent, such as toluene, benzene, xylol, and the like. The solution is prepared so that the solid resin content ranges between 20 and 60% solids. Prior to actual use the solution of the resin is diluted with a sufficient volume of a lower alkyl chlorinated hydrocarbon, such as, for example, chloroform, carbon tetrachloride, ethylene chloride, 1,1-dichloroethane, 1,1,1-trichloroethane, and the like to give a solution having a solid content ranging from 0.5 to 1.0%. A suitable volume of such diluted solution may be employed per 1 lb. of iron powder to yield a solid resin coating ranging from 0.1 to 0.5% by weight of the iron powder.

After the mixing is complete, the hydrocarbon and chlorinated solvents are allowed to evaporate either at room temperature or slightly elevated temperature until a dry powder remains. The iron powder coated with the dry silicone resin is then charged into any suitable oven and heated at 450–600° C., preferably at 550° C. for a period of time ranging from 2 to 10 hours in a stream of hydrogen gas of at least 99% purity with no more than 0.2% oxygen (by volume) at a flow rate to give a total of hydrogen of 3 to 6% by weight of the weight of the powder charged. During this heating treatment the silicone resin may decompose to silicates. Throughout the reduction treatment no appreciable sintering occurs and the amount of coarse particles after slight milling is very negligible. This is the conventional reduction treatment which yields an iron powder of less than 0.1% carbon, 0.3% oxygen, and 0.1% nitrogen with small traces of other elements. The powder, after reduction, is then ready for working up into high frequency cores.

The resulting powder usually passes through a sieve of 200 meshes per linear inch without difficulty. Under more extreme conditions, a certain small fraction of coarse powder may result. This fraction can easily be broken up to the same size by mild milling. The powder is then completely finished and ready to be mixed with a binder and so to be worked up into high frequency electronic cores in the conventional way.

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, obtainable with carbonyl iron type L. The 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 powder also yields a permeability of above 100 at the molding pressure of 100 tons/in.².

The particular action by which the resin silicone treatment improves the electromagnetic properties of the metal powder is not clearly known nor has it been definitely ascertained. It is believed, however, that the surface layer of silicone resins prevents sintering due to the formation of a uniform thin surface film on each iron particle which does not cohere during the reduction treatment. This be-

lief has not been confirmed. The fact does remain that the surface treatment prior to reduction materially improves the electromagnetic properties of the powder as will subsequently appear. Furthermore, due to the fact that the surface treatment is performed under mild, agitating conditions, an absolutely uniform effect is obtained without resorting to additional operations, such as washing, filtering, and grinding, which must always be employed when using solutions as the treating agents.

The particular operational advantages of the surface layer treatment in accordance with the present invention are manifold. For example, the reduction furnace may be filled to capacity, thus keeping yields high. The trays or pans may be emptied easily and safely since the powder is loose and freely flowing. No crushing, pulverizing, or milling is necessary. The powder readily passes through the required sieves, thus saving processing and maintenance cost. There are no clustered, deformed, or work-hardened particles in the powder which results in much better compressibility, permeability, and Q values than were heretofore obtainable. The layer on the particles put on before the reduction or decarburization treatment is preserved throughout the treatment and subsequent thereto. This occurs despite the fact that the nature of the particles and hence of the powder has changed radically. The change is indicated by the fact that the magnetic permeability rises from below 20 to above 100. In spite of this change the coating still acts as an insulator thereby rendering unnecessary any of the customary insulation treatments applied to finished heat treated powders. The elimination, in accordance with the present invention, of the heretofore unavoidable insulation treatment of a finished powder is of technical and commercial advantage and represents a saving and hence makes the new powder more attractive.

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

Example

100 grams of iron powder obtained by decomposition of iron pentacarbonyl between 250–300° C. and having a carbon content of 0.7% were placed in an electrical stirrer-agitator bowl of 500 cc. capacity. To the iron powder were added 0.17 gram of silicone resin varnish purchased on the open market under the brandname of Dow-Corning #2103 which contained 0.10 gram of solids and which was diluted with 20 cc. of carbon tetrachloride. Stirring was maintained after the addition of the silicone varnish until each particle of iron was completely coated. This took on the average between 15 to 30 minutes. During that time the carbon tetrachloride was allowed to evaporate until a dry powder remained. The dry powder was then charged in a boat, placed in a laboratory oven, and heated at 550° C. for 3 hours in an atmosphere of hydrogen (over 99% purity) at a uniform rate so as to give a total of hydrogen of 5% (by weight) of the weight of the powder. After discharge, the powder having a carbon content of 0.015% was screened through a 200-mesh sieve leaving a total of 0.7% of coarse residue above the sieve.

A portion of the 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 solution 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

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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.² 101.
molding pressure.
(b) Eddy current loss coefficient 0.09×10^{-6} ohms per henry
at 50 tons/in.² (no insulation and cycles-per-second
treatment). squared.
(c) Residual loss coefficient 8.5×10^{-3} ohms per henry and
cycles-per-second.

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 leakage 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.

Partially dehydrated methyl silicone resin, partially dehydrated phenyl methyl silicone resin, and the resin polymers of dimethyl dichlorosilane, diethyl dichlorosilane, trimethyl chlorosilane and triethyl chlorosilane when employed as the coating material, as in the example, gave the same satisfactory electromagnetic results.

For comparison purposes, corresponding values of com-

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mercial reduced carbonyl iron powders were determined and are listed in table form below. These were made by starting with the same iron powder, but no surface treatment 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.

10	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
15	(b) Eddy current loss coefficient at 50 tons/in. ² (no insulation treatment) $\times 10^{-6}$ ohms per henry and cycles-per-second squared	0.25	0.07	1.0	0.16
	(c) Residual loss coefficient $\times 10^{-3}$ ohms per henry and cycles-per-second	11	11	19	19

The foregoing data clearly demonstrate the advantages of the 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 the art that many variations may be made therein without departing from the spirit thereof. For example, instead of employing carbon tetrachloride as the solvent diluent for the silicone resins or as a dispersing medium for the iron phosphate and sodium tetrasilicate, any volatile organic liquid may be employed, preferably the lower alkyl chlorinated hydrocarbons disclosed above. Accordingly, the scope of my invention is to be limited only by the following claims.

35 I claim:

1. The process of improving the electromagnetic properties of carbonyl iron powders which comprises subjecting comminuted, pulverulent iron powder obtained by thermal decomposition of pentacarbonyl iron having a carbon content of at least 0.1% to a coating treatment with a silicone resin, reducing the treated powder with hydrogen at a temperature ranging between 450° C. and 600° C. for a period of time until the carbon content of the iron powder is reduced so as not to exceed 0.05% by weight of the treated powder, mixing the reduced powder with a binder and then forming a core from said mixture.

2. The process according to claim 1, wherein the treatment is conducted with partially dehydrated methyl silicone resin.

3. The process according to claim 1, wherein the treatment is conducted with partially dehydrated phenyl methyl silicone.

4. The process according to claim 1, wherein the treatment is conducted with a silicone resin of dimethyl dichlorosilane.

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