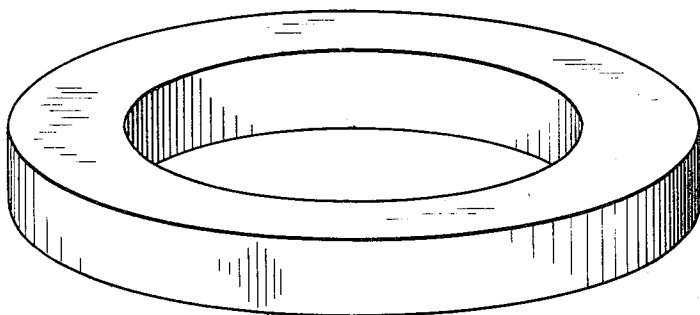


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PULVERULENT IRON OF IMPROVED
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PULVERULENT IRON OF IMPROVED ELECTROMAGNETIC PROPERTIES

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The present invention relates to powdered carbonyl iron and to shaped metallic articles prepared from such carbonyl iron for use in electromagnetic devices, and more particularly to magnetic cores produced from iron powder derived from the thermo-decomposition of iron carbonyl. A more particular feature of our invention is the production of powdered iron magnetic cores which combine both high permeability and low eddy current losses at frequencies up to several megacycles. Our invention provides new cores having permeabilities of over 50 without the hitherto unavoidable corresponding high eddy current losses.

Electromagnetic cores prepared from powdered carbonyl iron have been suggested for use in a great variety of coils. The usual purpose of the heretofore known cores has been either merely to assure a high Q value or to provide an inductance control or both. With the advent of improved communication equipment, for example, in direction finder loop antennae, it has become necessary that electromagnetic cores should also provide a high magnetic flux which means that the cores must have a high magnetic permeability and low losses.

Maintaining low eddy current losses, the highest permeability so far obtainable with cores prepared from heretofore known magnetic powders is below 40 and usually ranges from about 10 to 30. Recently, for example, T. Oddie, in a paper entitled "Magnetic measurements of iron powders" (Journal Scientific Instruments, London, page 154, September 1944), describes a variety of radio cores in which permeabilities range from 1.37 to 30.1.

In U. S. Patent 1,838,831, there is described the treatment of metallic powders obtained by the thermo-decomposition of iron carbonyl which involves subjecting such iron powder to a thermo-treatment in an atmosphere of reducing gas prior to making up the cores. It is stated that the permeability of the powder is improved. The one example in this patent discloses the treatment of iron powder, obtained by the decomposition of iron carbonyl, for 18 hours at 500° C. with a current of hydrogen. Such a treatment causes a loss of the original shape of the iron powder particles due to their sintering together to form large particles. Such sintered particles cannot be brought back to the spherical shape and size of the original particles. While cores prepared from such powders as produced by the process disclosed in this patent are said to have a higher permeability, they exhibit considerable eddy current losses.

U. S. Patent 1,735,405 points out on page 1, column 1, lines 1 to 27, that the aforesaid heat

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treatment in a reducing atmosphere, while reducing the carbon and oxygen in the iron, causes sintering, and that when carrying out the process on a large scale it is not always possible to bring the whole of the material back to the original small grain size and spherical shape of the original particles. Especially when the material has been heated to high temperatures, such as from 500 to 600° C., considerable amounts, as much as 30% and more, of screening residues are left over after grinding which are not directly applicable for the purposes required, the patent states. The patent proposes a two stage operation involving temperatures of 500° C. and over, which is still attended by sintering "restricted within moderate limits." The resulting iron powder obtained when crushed down in a mill, it is said, will pass through a sieve with 4900 meshes per square centimeter, leaving behind practically no residue. The powder is stated to have a carbon content up to 0.5% and a permeability of between 25 and 32.

In U. S. Patent 1,783,560 and U. S. Patent 1,783,561, there is disclosed the production of magnetic cores manufactured from carbonyl iron powders which have been treated with an insulating and bonding material and then molded under a pressure of about 7,000 kilograms per square centimeter. In U. S. Patent 1,783,560, the specific gravity of the resultant core is disclosed as being 6.52 and, it is stated, to possess a permeability of $\mu=38.6$. In U. S. Patent 1,783,561, the corresponding figures are given as 6.4 and 35.2.

It has been recognized that in the production of powdered iron cores, an increase in density results in a higher initial permeability. However, while increasing the density results in a greater permeability, the increase in the density at the same time is also accompanied by a corresponding increase in eddy current losses which is highly disadvantageous. Thus, while it is often essential to use magnetic cores of the highest possible permeability, there is a definite limitation imposed upon the permeability of magnetic materials in alternating electromagnetic fields by the appearance of eddy current power losses which increase with an increase in density of the core. This is particularly true in the case of high frequency electromagnetic fields. As a result, to avoid the appearance of such losses, it has been necessary to sub-divide the magnetic materials as, for example, by laminating the core. While this reduces the eddy current losses, it also decreases the overall permeability. Thus, it has not been heretofore possible to produce cores combining the features of high permeability and low losses by increasing the density of the core.

It is among the objects of our invention to produce a new powdered carbonyl iron and shaped metallic articles therefrom particularly useful as cores in electromagnetic devices which, although possessing high densities combine both high permeability and low power losses at high frequencies. According to our invention, it is possible to produce powdered iron cores having initial magnetic permeabilities of from 40 to 72 with relatively low eddy current power losses. Thus, we have succeeded in producing powdered iron cores having permeabilities of from 40 to 72 with comparatively low eddy current loss coefficients of from 0.6 to 7.0×10^{-7} ohms per henry and cycles-per-second-squared.

Our invention exhibits its greatest advantages and effectiveness in making possible the production of high density cores having permeabilities of over 50 without the hitherto unavoidable corresponding high eddy current losses.

The new cores are prepared from a new, soft carbonyl iron powder of small particle size using a suitable insulating material for bonding, which is efficient as such even in very small quantities. More particularly, according to our invention we have found that powdered iron cores can be obtained with effective permeabilities higher than that heretofore obtained and without a corresponding increase of eddy current power losses, by preparing such cores from a pulverulent iron obtained from the thermo-decomposition of iron carbonyl, provided the powdered iron consists substantially of spherical particles of less than 12 microns in diameter and has a total carbon content not exceeding 2.9 in 10,000 parts by weight. Thus, a powder whose carbon content ranges from about 0.01 to 0.029% by weight and the number-average diameter of the particles is about 6-10 microns has been found highly effective for the production of our new electromagnetic cores.

In the preparation of the cores, the iron powder described can be insulated and coated in any convenient way with a suitable insulating and bonding material and then compressed to flawless compacts having initial magnetic permeabilities of up to 72 with relatively low eddy current power losses. The density of such compacts is as high as 7.50 grams per cubic centimeter. It is also possible to process the new iron powder without coating into compacts which are called "green briquettes" having even higher densities as, for example, up to 7.55 grams per cubic centimeter and which after a sintering treatment exhibit excellent magnetization characteristics.

The new carbonyl iron powder differs from heretofore commercial grades in the following properties:

Grade	Carbon Content Per Cent	Weight-Average Diameter of Particles in Microns
L.....	0.005-0.03	20
C.....	0.03-0.12	10
E.....	0.65-0.30	8
New Powder.....	0.01-0.029	10

L, C and E denote heretofore known commercial grades of carbonyl iron powders.

The new carbonyl iron powder from which our new cores are prepared can in general be produced as follows: Iron carbonyl is decomposed in the heated free space of the decomposition vessel according to the procedure of Patent No. 1,759,659. The individual particles of the iron powder so

obtained have a rounded or substantially spherical shape. The average diameter of the particles ranges from about 6-10 microns, while the carbon content of the iron is from 0.5 to 1.2%.

The carbonyl iron so obtained is subjected to a reduction treatment to reduce the carbon content to not over 2.9 parts per 10,000, under such conditions of time and temperature which prevent sintering and maintain substantially the spherical shape and small size of the original particles. Such reduction with preservation of the original small size and spherical shape of the original particles can be carried out by maintaining the temperature of treatment with the reducing gas within a range of about 380° C. to about 430° C. for a length of time ranging from about 7 to about 12 hours, depending on the temperature and the concentration of the reducing gas.

As the reducing gas, we prefer to employ hydrogen, although any other suitable reducing gas, such as, ammonia may also be employed. The amount of reducing gas employed is at least that required to reduce the carbon content within the range of 0.01 to 0.029%, but it is preferred to utilize an excess of the gas and control the length of treatment until the carbon content of the iron powder is reduced to the above specified range. For example, we prefer to employ from about 100-200% excess hydrogen.

After treatment with the reducing gas, the iron particles are subjected to a mild milling operation to break up any agglomeration of particles. This operation, performed preferably in a ball mill, is carried out so mildly that the original spherical shape and small size of the particles is maintained, and their conglomeration by impact avoided.

The iron powder is next shaped into cores. Any suitable insulating and bonding material may be employed in preparing the cores. For example, we have found to be highly advantageous for this purpose a butanol-soluble urea-formaldehyde resin of the baking enamel type. While the amount of insulating and bonding material employed may be varied, we have found it particularly advantageous, where high permeability is desired with relatively low molding pressure, that the amount of insulating and bonding material be relatively small. Thus, we have found it advantageous to employ the insulating material in a range of about 0.2-0.7% based on the weight of the iron. A highly preferred amount of insulating and bonding material is about 0.5% by weight. For example, a core having a permeability of 55 and an eddy current loss coefficient of 0.73×10^{-7} ohms per henry and cycles-per-second squared, and a density of 7.35 grams per cm.³ can readily be obtained from our new iron powder when employing about 0.5% of urea-formaldehyde as the insulating and bonding material and a molding pressure of 85 tons per square inch. Densities of over 7 have heretofore been very rarely obtained in powdered iron cores and such cores as have been obtained with such densities have been characterized by having high eddy current losses.

By utilization of iron powder in which the particles are rounded or spherical in shape and possess a diameter of less than 12 microns, and in which the carbon content does not exceed 0.029%, we have succeeded in obtaining a shaped metallic product which in spite of its high density and high initial permeability does not exhibit any substantial increase in eddy current losses as is exhibited by increasing the density of powdered

iron cores made from the heretofore known iron powders.

The following examples will further illustrate the method of preparing our new powder and the production of our new magnetic cores.

Example 1

Iron powder obtained by the thermo-decomposition of iron pentacarbonyl was reduced with hydrogen at a temperature of 425° C. for 7 hours. The reduced iron powder was then milled in a ball mill to break up any agglomeration of particles. The ball milling operation is performed in such a way that the original spherical shape and size of the individual particles is not impaired. This can be effected by carrying out the milling by a fractional operation in which the particles are removed from the mill at frequent intervals to prevent mutilation of their shape or conglomeration by impact.

The pulverulent iron obtained had a carbon content of 1.2 parts in 10,000, or 0.012%, and consisted substantially of particles with a diameter of about 10 microns.

The preparation of shaped articles and more particularly electromagnetic cores is illustrated by the following example.

Example 2

1000 parts of iron powder obtained as in Example 1 were mixed with 200 parts of a 2.5% solution of a butanol-soluble urea-formaldehyde condensation product in n-butyl alcohol. The alcohol was then evaporated from the mixture, and the coated powdered iron was heated to about 145° C. to polymerize or set the resin coating. The lumps of coated carbonyl iron were reduced to small grains by grinding. The grains so obtained and coated with the resin were formed into a ring in a mold using a pressure of 85 tons/in.² The resulting ring weighed 100 grams, had an outside diameter of 2.25 inches, an inside diameter of 1.5 inches, and a height of about 3/8 inch. The density of the ring was 7.35 grams per cm.³ The ring was kept for 30 minutes at 150° C. in air in order to increase its mechanical strength, and then wound toroidally with wire.

various A. C. frequencies (f) up to 1 megacycle. The apparent Q values, determined by direct measurement, were corrected in accordance with the characteristics of the measuring instrument to yield actual Q values. The cores were then wound as toroids with sufficient turns to yield an inductance (L) of 0.10 millihenry. The D. C. resistance (R_0) of the coil is measured with a Wheatstone bridge. 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 residual loss coefficient (c) was determined from the loss resistance at 1 and at 10 kilocycles, extrapolated to a flux density (B) of zero. The hysteresis loss coefficient (a) was obtained from measurements with an inductance bridge at various flux densities and constant frequency (10 kilocycles).

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 hysteresis loss, residual loss, and eddy current loss. This relationship is expressed by the equation $R_{eff} = R_0 + \mu L f (aB + c) + \mu e L f^2$, wherein the second term of the sum represents the hysteresis and residual loss resistances, and the last term represents the eddy current loss resistance, μe being the eddy current loss coefficient. Since all of the terms except μe can be calculated from the measurements indicated above, the value in ohms of the eddy current loss resistance (R_e) can be obtained by subtracting R_0 and the second term of the above expression from R_{eff} . The eddy current loss coefficient (μe) is then calculated as the quotient of R_e/Lf^2 . Thus, the units of the eddy current loss coefficient are ohms per henry and cycles-per-second squared.

The following table illustrates the relative properties of cores prepared from our new carbonyl iron powder as compared with cores prepared from known iron powders.

Core	Permeability	Eddy current loss coefficient ohms/henry cps. ²	Particle size weight avg. diameter microns	Density	Carbon content, percent (by weight)	Molding Pressure, T. S. I.
A-----	70	7.0×10^{-7}	10	7.42	0.012	85
B-----	55	0.73×10^{-7}	10	7.35	0.012	85
C-----	40	0.66×10^{-7}	10	6.83	0.012	50
D-----	39	1.0×10^{-7}	20	6.40	0.02	50
E-----	42	1.69×10^{-7}	13	6.90	0.005	85
F-----	16.5	0.08×10^{-7}	8	5.24	0.73	60

The coil thus obtained was subjected to a series of standard measurements which showed the initial magnetic permeability of the core to be 55. Its eddy current power loss coefficient was found to be 0.73×10^{-7} ohms per henry and cycles-per-second squared.

The aforesaid standard method and the calculations employed in determining "initial permeability" and "eddy current loss coefficient" are 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 direct measurement of the apparent Q value (quality factor) of the core, using a Q -meter while the core is inserted in a solenoid energized by

In the above table, cores A, B and C are cores prepared from our new carbonyl iron powder. Core D is prepared from a carbonyl iron powder in which the carbon content is 0.02% and the diameter of the particles 20 microns. The particles in this powder are to a large extent sintered masses of spherical particles. Core E is prepared from one of the best grades of iron powder obtained by the hydrogen reduction of iron oxides. Core F is prepared from the most commonly used non-reduced iron powder as prepared by the thermal reduction of iron carbonyl.

Thus, it is evident that none of the heretofore known iron powder cores of which examples are given in the table combine high permeability and low losses as do our novel powder cores. Our

new cores exhibit their greatest advantages and are most effective, particularly when they are of the high density type. Thus, cores A and B prepared at 85 tons per square inch have extremely high permeability, density and low eddy current loss. This is contrary to what would be expected since high density has heretofore been unavoidably accompanied by corresponding high eddy current losses. Core C prepared at a lower pressure, while still possessing a permeability of 40, has at the same time, an even lower eddy current loss. The known cores D and E, while having a permeability similar to core C and a similar density, possess considerably greater eddy current loss. Core F, although prepared at a pressure of 60 tons per square inch has an extremely low permeability and low density.

A simple core combining high magnetic permeability with low eddy current losses and made according to the method of the present invention, is illustrated in the accompanying drawing.

From the description herein given it will be evident that our invention provides both a novel carbonyl iron powder and novel shaped metallic articles which solve the problem of combining high magnetic permeability and low losses, and more particularly high density cores with permeabilities of over 50 combined with low eddy current losses.

It is to be understood that the new iron powder, instead of being utilized for the production of magnetic cores, is also well suited for the production of various sintered parts, such as for the manufacture of alloys and combinations involving non-metallic materials as, for instance, carbon steel compacts.

We claim:

1. In a method of producing powdered iron which combines high permeability and low eddy current losses when formed into shaped articles, the step, which comprises reducing iron powder obtained by the thermo-decomposition of iron carbonyl, the particles of which are spherical in shape and have an average diameter of less than 12 microns, with a reducing gas of the class consisting of hydrogen and ammonia at a temperature sufficiently high to reduce the carbon content of the iron powder by reaction of carbon with said gas, but not exceeding 430° C., and for a period of time so limited as to avoid sintering of the particles and to maintain their original shape and size, said treatment being carried out until the carbon content of the iron is reduced so as not to exceed 0.029% by weight of the powder.

2. In a method of producing carbonyl iron which combines high permeability and low eddy current losses when formed into shaped articles, the step which comprises reducing iron powder obtained by the thermo-decomposition of iron carbonyl and the particles of which are spherical in shape and have an average diameter of less than 12 microns with hydrogen at a temperature of from about 380-430° C. for about 7-12 hours, said treatment reducing the carbon content of the iron so as not to exceed 0.029% by weight of the powder.

3. In a method of producing carbonyl iron which combines high permeability and low eddy current losses when formed into shaped articles, the step which comprises reducing iron powder, the particles of which are spherical in shape and have an average diameter of 6-10 microns, said powder being obtained by the thermo-decomposition of iron carbonyl, with hydrogen at

a temperature of about 425° C. for about 7 hours, said treatment reducing the carbon content of the iron from 0.01% to 0.029% by weight of the powder.

4. Powdered carbonyl iron in which the particles are spherical in shape, having a carbon content not exceeding 0.029% by weight of the powder and an average particle diameter of less than 12 microns said powder being capable of being molded into cores having a permeability of from about 40-72, and an eddy current loss coefficient of about $0.6-7.0 \times 10^{-7}$ ohms per henry and cycles-per-second-squared.

5. A shaped article having an initial permeability of at least 40 consisting substantially of carbonyl iron powder having a carbon content not exceeding 2.9 parts by weight per 10,000 parts, said iron powder being in the form of particles of spherical shape having a diameter of substantially less than 12 microns.

6. A powdered iron core having an initial magnetic permeability of from 40-72 and consisting substantially of carbonyl iron powder in which the particles have their original spherical shape and size, said carbonyl iron powder having a carbon content not exceeding 0.029% by weight, and an average particle diameter of substantially less than 12 microns.

7. A powdered iron core having an initial magnetic permeability of at least 50 and an eddy current loss coefficient of from 0.6 to 7×10^{-7} , and consisting substantially of carbonyl iron powder in which the particles have their original spherical shape and size, said carbonyl iron powder having a carbon content from 0.01% to 0.029% by weight and an average particle diameter of 6-10 microns; and an insulating binder coating the particles of said core.

8. A method of preparing a powdered iron core which comprises coating the particles of carbonyl iron powder with an insulating binder in amounts of from 0.2-0.7% based on the weight of the iron, said carbonyl iron powder being obtained by the thermo-decomposition of iron carbonyl to iron powder of which the particles are spherical in shape and have an average diameter of less than 12 microns, followed by the reduction of the resulting iron by means of hydrogen at a temperature sufficiently high to reduce the carbon content of the iron powder by reaction of carbon with hydrogen, but not exceeding 430° C., and for a period of time so limited as to avoid sintering of the particles and to maintain their original spherical shape and size, said treatment being carried out until the carbon content of the iron is reduced so as not to exceed 0.029% by weight of the powder, and then molding the mixture under pressure to the desired shape to form a core having a permeability exceeding 50 and an eddy current loss coefficient of from 0.6 to 7×10^{-7} ohms per henry and cycles-per-second-squared.

9. A method as in claim 8 in which the insulating binder is a butanol-soluble urea-formaldehyde condensation product.

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The following references are of record in the file of this patent:

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Number	Name	Date
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