

May 31, 1960

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2,938,781

PRODUCTION OF MAGNETIC IRON PARTICLES

Filed Dec. 27, 1957

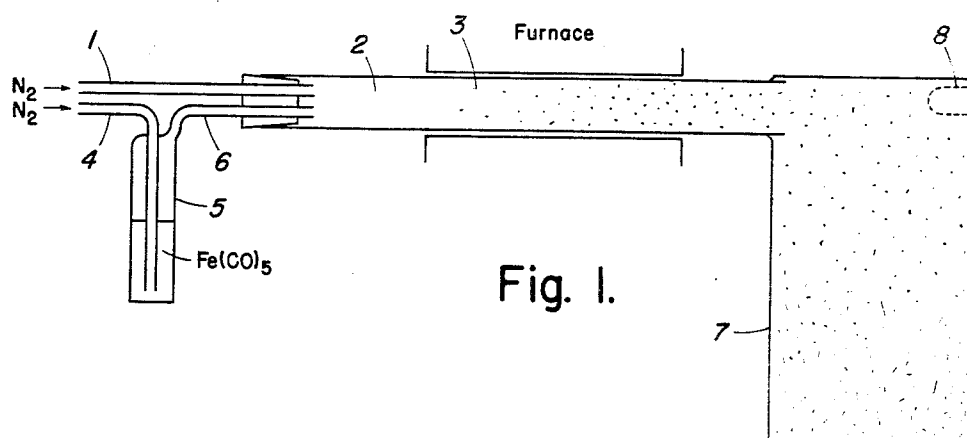
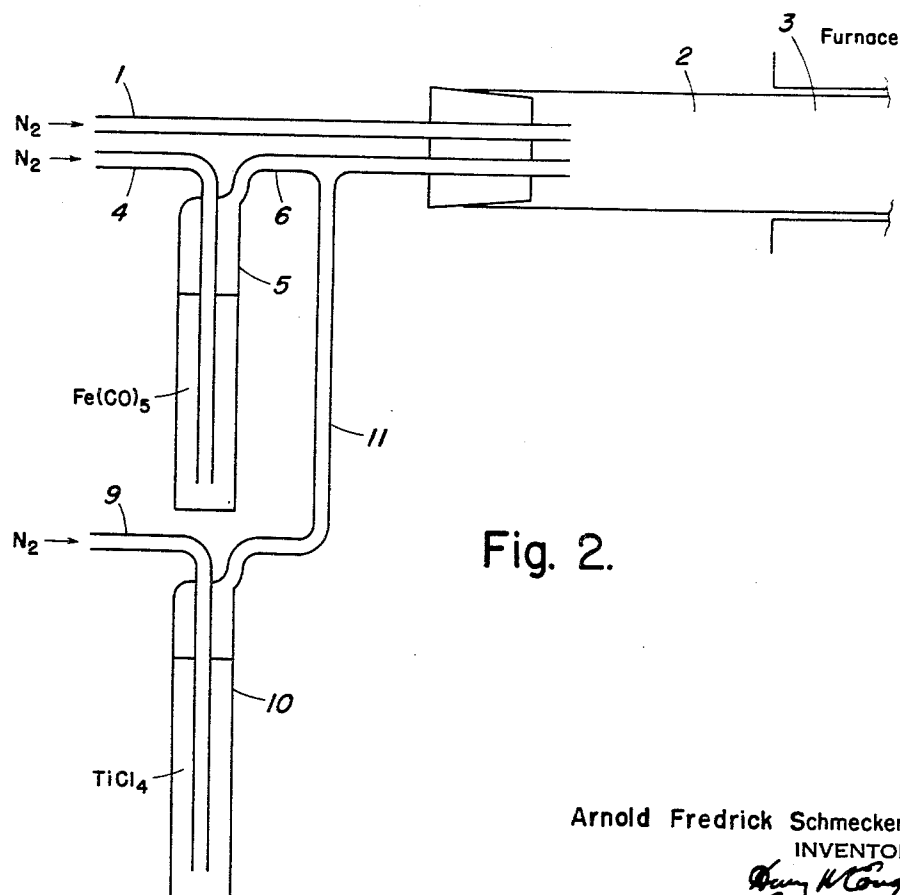


Fig. 2.

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PRODUCTION OF MAGNETIC IRON PARTICLES 5

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Filed Dec. 27, 1957, Ser. No. 705,700

10 Claims. (Cl. 75—5)

This invention relates to the production of finely divided iron particles and more particularly to the decomposition of iron carbonyl in the production of finely divided iron particles having optimum magnetic properties.

The theoretical considerations involved in the production of permanent magnets from ultrafine iron powder is well known, a discussion thereof having been presented for example in an article by Kopelman, "Permanent Magnets From Ultrafine Iron Powder," Electrical Engineering, pages 447 to 451 (May 1952). As pointed out in this article, permanent magnets of optimum coercive force are obtainable with iron particles which are highly elongated single domain ellipsoids of about 160 Angstrom units (.016 micron) in size.

It is well known that the decomposition of iron carbonyl in the hot free space of a decomposer leads to the formation of iron in fine particulate form which may be employed for making magnetic cores and other similar articles. The use of such a method for the production of iron particles having the above mentioned optimum particle size and shape for the production of permanent magnets has, however, not been completely satisfactory. Most such processes have yielded particles which do not have the required size, size distribution and/or shape, or which are procedurally disadvantageous by reason of cost, lower efficiency, difficulty in operation and the like.

It is an object of this invention to provide a novel process for the thermal decomposition of iron carbonyl which will produce iron particles having improved magnetic properties, another object of this invention is the provision of such a process which may be carried out at lower cost, with higher efficiencies, and/or without undue difficulty. Other objects and advantages will appear as the description proceeds.

The attainment of the above objects is made possible by the instant invention which comprises a process for producing finely divided iron particles by continuously forming a gaseous mixture containing iron carbonyl vapor and an inert gas in volumetric proportions ranging between 1:100 and 1:1000, and preferably about 1:125 and 1:500, at a temperature below the decomposition temperature thereof, and passing said mixture through a thermal decomposition zone heated to a temperature of about 200–800° C., and preferably about 300–450° C. It has been found that the process of this invention enables the production of extremely fine elongated iron particles which, because of their size, size distribution and shape characteristics, may be pressed into a core without or with a binder such as wax, resins, or the like, such core having a coercive force of 400 oersteds or more and a remanence of 0.5 kilogauss or more. Coercive forces of this magnitude could only be obtained with iron particles having the aforementioned characteristics for producing permanent magnets of optimum coercive forces, or in close approximation thereto.

As pointed out above, previously employed methods

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for producing iron powder by the thermal decomposition of iron carbonyl have in general been ineffective for producing optimum permanent magnetic characteristics. The particle size distribution of the powders produced by such processes have ranged from about 2 to 20 microns. In U.S. 2,674,528 there is disclosed an improved process for thermally decomposing iron carbonyl by the use of sound waves, the size of the particles so produced ranged from about 0.5 to 1.5 microns in diameter. Such particles obviously will not yield the desired magnetic characteristics, since as pointed out above, particles of about .016 micron in size are necessary. It has also been previously proposed to use an inert gas diluent, but only in smaller proportions and/or in a different process, whereby the attainment of optimum particle characteristics for high coercive forces is prevented.

In carrying out the process of the instant invention, it is important that the admixture of the inert gas with the iron carbonyl vapor be carried out at temperatures below the decomposition temperature thereof, preferably at room temperature (20°–25° C.), below 200° C. under ambient conditions. Thus, it has been found that when a stream of inert gas carrying iron carbonyl vapor is fed into a stream of inert gas maintained at decomposition temperatures, particles having a size ranging from about .007 to .009 micron are obtained, which size is below the desired optimum particle size. The production of such unduly small particles may be ascribed to instantaneous decomposition reaction taking place at the moment of introduction of the iron carbonyl vapor into the hot inert gas. In the instant process, the dilute mixture of inert gas and iron carbonyl vapor is formed prior to subjection thereof to decomposition temperatures, whereby particles of improved size and shape characteristics are obtained in the hot decomposition zone.

As a further feature of this invention, it has been found that further improved magnetic properties may be obtained when preformed liquid or solid nuclei are introduced into the gaseous mixture prior to subjection thereof to decomposition temperatures. Non-volatile solid nuclei may be employed as formed by the substantially instantaneous reaction of a very small amount of a reagent, capable of reacting substantially instantaneously with the iron carbonyl vapor at lower temperatures, with the iron carbonyl vapors, prior to subjection to decomposition temperatures. As examples of such reagents, there may be mentioned halogens such as chlorine, bromine and iodine, nitric acid, hydrochloric acid, and the like. Other solid particles which may be employed as nuclei include metal oxides, salts, sulfides, carbonates, or the like. These solid particles may be preformed and introduced into the preformed gaseous mixture, or they may be formed by introducing the reagents into the inert gas or the stream of iron carbonyl vapors being fed into the inert gas at below decomposition temperatures. Such solid nuclei, their proportions and manner of use are adequately disclosed in U.S. 2,776,200, to which reference is here made for such adequate disclosures.

Volatile liquid metal halides may also be employed as nuclei such as arsenic trichloride, titanium or silicon tetrachloride, phosphorus or boron trichloride or tribromide, titanium tetrabromide, and the like. Only a very small quantity of such nuclei is required, the maximum quantity to be employed in any particular instance being readily determinable by the consequent production of particles which do not have the desired size, size distribution and/or shape. Such volatile halides are previously admixed in the form of the vapors or as discrete

droplets into the carbonyl vapor at below decomposition temperatures in proportions of about 0.5 to 5% by weight of the carbonyl. The liquid halide in the free space of the decomposition zone decomposes and/or reacts with the carbonyl vapor to produce solid nuclei in situ for the desired promotion or catalyzation of the decomposition of the carbonyl to yield iron particles of the desired characteristics.

Solid nuclei may also be employed, which are produced by reaction of oxygen, as such or in the form of air, ozone, or the like, with the iron carbonyl to form iron oxide particles. This reaction may take place prior to or during the decomposition of the carbonyl vapor. Only about 0.1 to 1.0 volume parts of oxygen per 1,000 volume parts of iron carbonyl vapor should be employed.

As the inert gas to be employed in the instant invention, nitrogen is preferred but carbon monoxide may also be employed. When employing carbon monoxide as the inert gas, care should be taken to avoid pressures which may cause decomposition of the carbon monoxide, whereby finely divided carbon would be simultaneously produced. In general, the process may be carried out at subatmospheric up to about 10 atmospheres pressure, atmospheric pressure being preferred.

The process is operated continuously, the pre-formed mixture of iron carbonyl vapor and inert gas, with or without nuclei particles, being passed continuously through a zone maintained at a temperature of about 200 to 800° C. and preferably about 400 to 500° C. The retention time in the decomposition zone is relatively short, usually ranging from about .01 to 1 second, during which time very fine iron particles are formed of the desired characteristics, which frequently flock together into loose agglomerates of about .5 to 1 mm. diameter. These particles and/or flocks are carried out of the exit end of the decomposition zone in the inert gas stream and may be readily collected in a settling chamber, or by passing the gas stream containing the particles and/or flocks through a washing tower with benzene or the like, or by magnetic means. From the settling chamber, the inert gas may be vented through a filter bag or narrow mesh screen or other suitable type of separator.

The iron particles formed are pyrophoric in air and should accordingly be stored and handled in an inert atmosphere prior to molding or pressing into magnetic cores or plugs. They may be pressed or molded in known manner, without or with the usual binders or other suitable treatments and/or additives, preferably in a magnetic field, for producing pressed or molded cores which, when magnetized by subjection to a suitable magnetic field, for example 10 kilogauss or the like, yield permanent magnets having high coercive forces and remanences.

It will be understood that up to about 35% of the iron carbonyl vapor subjected to decomposition in accordance with this invention may be replaced by cobalt carbonyl vapor, whereby the magnetic properties of the product may be further improved.

The decomposition reaction vessel employed in the instant process may be similar to those commonly employed hitherto in carrying out the decomposition of iron carbonyl vapors to carbonyl iron in the hot free space therein, with whatever modifications may be necessary to carry out the process in accordance with the requirements of this invention. The reaction chamber may be heated in any desired manner, as for example, by electrical resistance wires, by jackets containing heated gases, liquids or superheated steam or the like.

The following examples, in which parts are by weight unless otherwise indicated, are illustrative of the instant invention and are not to be regarded as limitative.

Example 1

Figure 1 in the attached drawings illustrates the ap-

paratus employed in carrying out the process of this example. In carrying out the process, a stream of about 7 liters per minute of nitrogen at room temperature is blown through tube 1 into the premixing chamber 2 of a cylindrical electric resistance furnace 3, which is about 2" in diameter and 30" long. A second stream of about 0.8 liter per minute (48 liters per hour) of nitrogen at room temperature is passed through tube 4 into liquid iron pentacarbonyl at room temperature in container 5. From container 5 the stream of nitrogen carrying 10 grams per hour of iron carbonyl vapors is conducted through tube 6 into premixing chamber 2. In this premixture, the carbonyl vapor is diluted by the nitrogen at a ratio by volume of 1:410. The furnace is heated to 300° C. By decomposition of the iron pentacarbonyl, very fine iron particles are formed which frequently flock together into loose agglomerates of about .5 to 1 mm. diameter. The particles and/or flocks are carried out of the furnace by the gas stream and are collected in settling chamber 7, which may be a polyethylene bag. From the settling chamber, the gas is vented through a narrow mesh screen 8.

The flocks, which are pyrophoric in air, can be filled into a mold under inert atmosphere and can be pressed into a cylindrical plug of $\frac{3}{8}$ " diameter and $\frac{3}{4}$ " length. Binders such as phenolformaldehyde resins or wax or another type of binder may be added to the material before pressing. The pressed plug is magnetized by a field of 10 kilogauss.

The fourth quadrant of the sheared hysteresis loop of the magnetic material in the plug and the coercive force and the fraction of the remanence corresponding to the unknown degree of shearing of the hysteresis loop are determined by a well known method. The current induced into a circuit with an inductance coil is measured when the plug is introduced rapidly into the inductance coil with the inductance coil situated in a magnetic field of practically zero and then in magnetic fields with increasing strengths opposite to the magnetic field of the plug. The current induced is measured with a ballistic galvanometer.

Coercive forces of 400-420 oersteds and various "sheared" remanences of about 1 kilogauss, depending on the density of the plug, are observed.

Example 2

Figure 2 in the attached drawing illustrates the apparatus in which the process of this example is carried out. This process is carried out in the same manner as that of Example 1 except that the second stream of nitrogen is raised to 1.9 liters/min. (114 liters/hour) and a third stream of 0.1 liter/min. (6 liters/hour) of nitrogen at room temperature is passed through tube 9 into liquid titanium tetrachloride in container 10, and the stream of nitrogen carrying about 1 gram/hour of titanium tetrachloride passes out through tube 11 into tube 6. In the premixture the carbonyl vapor is diluted by nitrogen at a ratio of 1:134 by volume. In this process the furnace is heated to a temperature of 450° C., and a finely divided iron powder is formed which when pressed into a plug and measured as described in Example 1 above, shows a coercive force of 600 oersteds.

This invention has been disclosed with respect to certain preferred embodiments, and there will become obvious to persons skilled in the art various modifications, equivalents or variations thereof which are intended to be included within the spirit and scope of this invention.

I claim:

1. A process for producing finely divided iron particles comprising continuously forming a gaseous mixture containing iron carbonyl vapors and an inert gas in volumetric proportions of about 1:410, at a temperature below the decomposition temperature thereof, and passing said mixture through a thermal decomposition zone heated to a temperature of about 200 to 800° C.

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2. A process as defined in claim 1 wherein said inert gas is nitrogen.

3. A process as defined in claim 2 wherein said zone is heated to a temperature of about 300° C.

4. A process for producing finely divided iron particles comprising continuously forming a gaseous mixture containing iron carbonyl vapors and an inert gas in volumetric proportions ranging between 1:100 and 1:1000, at a temperature below the decomposition temperature thereof, and passing said mixture in the presence of inert nuclei particles through a thermal decomposition zone heated to a temperature of about 200 to 800° C.

5. A process as defined in claim 4 wherein said inert gas is selected from the group consisting of nitrogen and carbon monoxide.

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6. A process as defined in claim 4 wherein said inert gas is nitrogen.

7. A process as defined in claim 4 wherein said inert gas is carbon monoxide.

8. A process as defined in claim 4 wherein said inert nuclei particles are derived from titanium tetrachloride.

9. A process as defined in claim 8 in which said inert gas is nitrogen.

10. A process as defined in claim 9 in which said zone is heated to a temperature of about 450° C.

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