



**EUROPEAN PATENT SPECIFICATION**

Date of publication of patent specification :  
**14.09.94 Bulletin 94/37**

Int. Cl.<sup>5</sup> : **H01F 1/36, H01F 1/37**

Application number : **90304167.1**

Date of filing : **18.04.90**

**Ferrite particles and ferrite resin composite for bonded magnetic core and process for their production.**

Priority : **19.04.89 JP 101204/89**  
**28.02.90 JP 50715/90**

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Date of publication of application :  
**24.10.90 Bulletin 90/43**

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Publication of the grant of the patent :  
**14.09.94 Bulletin 94/37**

Designated Contracting States :  
**DE FR GB NL**

References cited :  
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**EP 0 394 020 B1**

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## Description

The present invention relates to spherical ferrite particles suitable for a bonded magnetic core, a process for producing the particles and a ferrite resin composite containing the particles.

Ferrite particles and a ferrite resin composite are mainly used as a magnetic core material of an induction coil for various electronic machines such as a computer, communications apparatus and home appliances, and as a magnetic core material of a transformer.

A bonded magnetic core, which is superior to a sintered magnetic core in dimensional stability, processability and resistance to brittleness, is advantageous in that a small or thin core is realizable and mass production of cores having a complicated shape is easy. With the recent development of electronics, the demands for providing lighter-weight, miniaturized and higher-accuracy cores, which are to be produced by making good use of these advantages, have been increasing.

A bonded magnetic core is generally produced by kneading a magnetic material with a resin such as nylon and phenol, and molding the resultant mixture by compression molding or injection molding.

As the magnetic material, an oxide material such as Mn-Zn ferrite and Ni-Zn ferrite is used. Such an oxide magnetic material is generally obtained by mixing a main raw material such as  $\text{Fe}_2\text{O}_3$ , MnO, ZnO and NiO in advance by wet or dry blending so as to have a desired composition, granulating the resultant mixture into particles having a diameter of about several mm to several ten mm, calcining the obtained particles and pulverizing the calcined particles into particles having an average particle diameter of several  $\mu\text{m}$  to several hundred  $\mu\text{m}$ .

A bonded magnetic core is required to have a magnetic permeability which is as large as possible. This demand has been increasing with the recent demand for a bonded magnetic core having a higher capacity.

It is known that a bonded magnetic core is composed of a magnetic material combined with a resin such as nylon and phenol, as described above, and that various properties, in particular the magnetic permeability of the bonded core, have a closer relation to and are more influenced by the properties of the magnetic material used in comparison with a sintered core. Therefore, in order to obtain a bonded magnetic core having a large magnetic permeability, it is advantageous to use ferrite particles having a large magnetic permeability as a magnetic material.

With the recent tendency toward bonded magnetic cores having a higher capacity, demands for smaller, thinner and more complicated-molded products have been increasing. To satisfy such demands, it is important that a ferrite resin composite can sufficiently fill all parts of the mold. For this purpose, the ferrite resin composite is required to have excellent fluidity.

However, in the ferrite particles produced by mixing raw materials such as  $\text{Fe}_2\text{O}_3$ , MnO, ZnO and NiO, granulating the resultant mixture into particles having a diameter of about several mm to several ten mm, calcining the obtained particles at a high temperature and pulverizing the calcined particles in accordance with the above-described conventional method, the crystal grains grow as large as several hundred  $\mu\text{m}$  and become non-uniform. In addition, the crystal grains contain many pores. Due to the non-uniform crystal grains and the presence of many pores, the magnetic permeability is lowered. As a result the obtained ferrite particles have a small magnetic permeability as a magnetic powder. Furthermore, since the magnetic powder itself is in the form of angular particles due to the pulverization, the fluidity thereof is too poor for a suitable magnetic material for a bonded magnetic core.

A magnetic material suitable for obtaining a bonded magnetic core having a large magnetic permeability has been conventionally proposed.

For example, in the method described in JP-A-55-103705 (1980), mixed ferrite particles consisting of particle groups having different particle sizes of from 100  $\mu\text{m}$  to 5 mm in diameter, for example a large-particle group having a diameter of 400  $\mu\text{m}$  to 5 mm and a small-particle group having a diameter of 100 to 350  $\mu\text{m}$ , are used as a magnetic material for obtaining a molded product (bonded core) having a large initial magnetic permeability. However, since the mixed ferrite particles contain particles having a large diameter such as 5 mm, they are not ideally suitable as a magnetic material for a bonded magnetic core.

US-A-4,357,717 discloses spherical ferrite particles for use as a carrier in a dry process copying machine which have a particle diameter of, for example, 30 to 200  $\mu\text{m}$ .

EP-A-44,592 discloses pre-shaped ferrite bodies for use in the manufacture of electromagnetic components. These may be in the form of balls having a diameter of 0.6 to 1.2 mm.

The magnetic permeability and the fluidity of the ferrite resin composite for producing a bonded magnetic core are mainly dependent on the properties of the ferrite particles which are mixed with the base materials of a resin composite. The magnetic permeability of the ferrite resin composite has a tendency to increase with the increase in the magnetic permeability of the ferrite particles mixed. The fluidity of the ferrite resin composite has a tendency to become better as the average particle diameter of the ferrite particles mixed becomes small-

er and the surfaces of the particles become smoother. The magnetic permeability of the ferrite particles has a close relation to the average particle diameter and, hence, the magnetic permeability of the ferrite resin composite increases with the increase in the average particle diameter. On the other hand, when the average particle size of the ferrite particles increases, the fluidity of the ferrite resin composite is deteriorated.

As to the relationship between the magnetic permeability and the average particle diameter of the ferrite particles obtained by the conventional method, when the average particle diameter is about 100  $\mu\text{m}$ , the magnetic permeability is about 18, and when the average particle diameter is about 200  $\mu\text{m}$ , the magnetic permeability is about 23.

Therefore, in order to obtain a ferrite resin composite having a large magnetic permeability and an excellent fluidity, the ferrite particles mixed are required to have an appropriate average particle diameter which produces a large magnetic permeability and does not obstruct the fluidity, in particular, an average particle diameter of not more than 200  $\mu\text{m}$ , and to have as smooth a surface as possible.

In the research undertaken to provide ferrite particles which have a large magnetic permeability, an appropriate particle diameter and an excellent smoothness, the present inventors have noticed that in order to produce ferrite particles having the large magnetic permeability, it is necessary to obtain ferrite particles having uniform crystal grains and an appropriate grain size and which containing no pores, and that in order to obtain such ferrite particles, it is important to use spherical granules for calcination which satisfy all the following conditions: (1) pores are easy to diffuse in the ferrite particles, (2) the ferrite particles are easy to balance with the calcination atmosphere, and (3)-the ferrite particles easily receive heat uniformly. The present inventors have also paid attention to spray drying which is capable of causing granulation substantially in the form of spheres. As a result, it has been found that by dispersing and mixing a mixed powder for producing ferrite particles consisting essentially of 47 to 55 mol%, calculated as  $\text{Fe}_2\text{O}_3$ , of an iron oxide or iron oxide hydroxide powder, 10 to 23 mol%, calculated as  $\text{NiO}$ , of a nickel oxide powder and 25 to 40 mol%, calculated as  $\text{ZnO}$ , of a zinc oxide powder into and with water containing 0.2 to 1.0 wt% of a surfactant based on the weight of the mixed powder for producing ferrite particles so as to prepare a water-dispersed slurry having a slurry concentration of 40 to 60 wt%, spray-drying the resultant slurry so as to obtain the granules having an average particle diameter of 25 to 180  $\mu\text{m}$ , and calcining the obtained granules at a temperature of 1100 to 1350°C, the obtained nickel zinc ferrite spherical particles comprise crystal grains of 5 to 15  $\mu\text{m}$  average diameter, and have an average particle diameter of 20 to 150  $\mu\text{m}$  and a magnetic permeability of not less than 25.

The present invention provides spherical ferrite particles suitable for a bonded magnetic core, which particles comprise uniform crystal grains of from 5 to 15  $\mu\text{m}$  in average diameter and have an average particle diameter of from 20 to 150  $\mu\text{m}$  and a magnetic permeability of not less than 25;

the above magnetic permeability being the magnetic permeability of a molded product obtained by:

- a) press-molding the particles and polyvinyl alcohol under a pressure of 1 ton/cm<sup>2</sup> to form a cylindrical molded product having an outer diameter of 36 mm, an inner diameter of 24 mm and a height of 10 mm; and
- b) winding the molded product with a winding of 40 turns and measuring the magnetic permeability thereof with an impedance analyzer at a frequency of 1 MHz.

The present invention also provides a ferrite resin composite comprising ferrite particles as defined above and a base resin, said ferrite resin composite having a magnetic permeability of not less than 25;

the above magnetic permeability being determined by:

- a) press-molding granules of said ferrite resin composite under a pressure of 1 ton/cm<sup>2</sup> to form a cylindrical molded product having an outer diameter of 36 mm, an inner diameter of 24 mm and a height of 10 mm; and
- b) winding the molded product with a winding of 40 turns and measuring the magnetic permeability thereof with an impedance analyzer at a frequency of 1 Mhz.

The present invention also provides a process for producing ferrite particles as defined above, which comprises:

- (i) mixing a) from 47 to 55 mol%, calculated as  $\text{Fe}_2\text{O}_3$ , of an iron oxide or iron oxide hydroxide powder, b) from 10 to 23 mol%, calculated as  $\text{NiO}$ , of a nickel oxide powder and c) from 25 to 40 mol%, calculated as  $\text{ZnO}$ , of a zinc oxide powder and d) water containing from 0.2 to 1.0 wt% of a surfactant based on the total weight of the powders a), b) and c) so as to prepare a slurry having a slurry concentration of from 40 to 60 wt%,
- (ii) spray-drying the resultant slurry so as to obtain spherical granules having an average particle diameter of from 25 to 180  $\mu\text{m}$ , and
- (iii) calcining the obtained granules at a temperature of from 1100 to 1350°C.

In the accompanying drawings:

Figs. 1 to 6 are scanning electron micrographs (x 6500), in which

Figs. 1, 2 and 3 show the structures of the ferrite particles for a bonded magnetic core obtained in Examples

1, 2 and 4, respectively; and

Figs. 4, 5 and 6 show the structures of the ferrite particles obtained in Comparative Examples 3, 4 and 7, respectively.

The nickel zinc ferrite spherical particles of the present invention are produced from (a) an iron oxide or iron oxide hydroxide powder, (b) a nickel oxide powder and (c) a zinc oxide powder as starting materials. More specifically, the nickel zinc ferrite spherical particles are produced by (i) dispersing and mixing a mixed powder for producing ferrite particles of (a) 47 to 55 mol%, preferably 48 to 53 mol%, calculated as  $\text{Fe}_2\text{O}_3$ , of an iron oxide or iron oxide hydroxide, (b) 10 to 23 mol%, preferably 13 to 20 mol%, calculated as NiO, of a nickel oxide and (c) 25 to 40 mol%, preferably 27 to 39, calculated as ZnO, of a zinc oxide into and with (d) water containing 0.2 to 1.0 wt% of a surfactant based on the weight of the mixed powder to prepare a water-dispersed slurry having a slurry concentration of 40 to 60 wt%, (ii) spray-drying the resultant slurry so as to obtain granules having an average particle diameter of 25 to 180  $\mu\text{m}$ , and (iii) calcining the obtained granules at a temperature of 1100 to 1350°C.

The reason why the nickel zinc ferrite spherical particles having a magnetic permeability of not less than 25 are obtained according to the present invention is considered to be because they comprise uniform crystal grains of an appropriate size containing few pores.

Since the ferrite particles of the present invention are spherical, have appropriate sizes, and are not irregular, they have an excellent fluidity which facilitates the production of a molded product having a complicated shape when the ferrite particles are kneaded with a resin and molded, especially by injection molding.

The spherical ferrite particles of the present invention comprise 47 to 55 mol%, preferably 48 to 53 mol%, of  $\text{Fe}_2\text{O}_3$ , 10 to 23 mol%, preferably 13 to 20 mol%, of NiO and 25 to 40 mol%, preferably 27 to 39 mol%, of ZnO. Particles having a composition outside the above ranges are unfavorable for practical use because the magnetic permeability is apt to be lowered.

The spherical ferrite particles of the present invention are nickel zinc ferrite particles having an average diameter of 20 to 150 $\mu\text{m}$ , preferably 30 to 140  $\mu\text{m}$ , and comprise crystal grains of 5 to 15 $\mu\text{m}$ , preferably 5 to 13  $\mu\text{m}$ , average diameter. If the average particle diameter of the ferrite particles is less than 20 $\mu\text{m}$ , the growth of the particles is unfavorably insufficient. An average particle diameter of more than 150 $\mu\text{m}$  is also unfavorable because the crystal grains grow abnormally and many pores tend to remain therein, thereby lowering the magnetic permeability.

In order to obtain the ferrite particles for a bonded magnetic core according to the present invention, it is necessary to control the average particle diameter of the granules before calcination to from 25 to 180 $\mu\text{m}$ .

For this purpose, it is necessary to disperse and mix the mixed powder for producing ferrite particles into and with water containing 0.2 to 1.0 wt%, preferably 0.2 to 0.8 wt%, of a surfactant based on the weight of the mixed powder for producing ferrite particles, thereby obtaining a water-dispersed slurry having a slurry concentration of 40 to 60 wt%, preferably 40 to 55 wt%, and thereafter to spray-dry the resultant slurry. If the slurry concentration is less than 40 wt%, the spray-drying efficiency is lowered, which often leads to a reduction in productivity. If the slurry concentration is more than 60 wt%, it is difficult to supply and spray-dry the slurry and, hence, it is difficult to produce the ferrite particles of the present invention.

As the iron oxide, which is one of the starting materials of the present invention,  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  are usable. As the iron oxide hydroxide,  $\alpha\text{-FeOOH}$ ,  $\beta\text{-FeOOH}$  and  $\gamma\text{-FeOOH}$  are usable.

As the surfactant, surfactants generally used as a dispersant for a water-dispersed slurry, for example, alkali salts, amine salts and ammonium salts of anionic surfactants, lower fatty acid salts and hydrochlorides of cationic surfactants are usable. The amount of surfactant used is 0.2 to 1.0 wt% based on the weight of the mixed powder for producing ferrite particles in consideration of sphericity of the ferrite particles obtained.

The calcining temperature is 1100 to 1350°C. If the temperature is lower than 1100°C, it is difficult to obtain large crystal grains. If it exceeds 1350°C, abnormal growth of the crystal grains is accelerated, so that the crystal grains become unfavorably non-uniform and contain many pores.

The ferrite resin composite of the present invention is a mixture of the above-described nickel zinc ferrite spherical particles and a resin, and has a magnetic permeability of not less than 25 and an excellent fluidity.

The nickel zinc ferrite spherical particles of the present invention may be coated in advance with a coupling agent which is generally used as a surface treating agent, for example, a silane coupling agent, titanium coupling agent, aluminum coupling agent and zircoaluminate coupling agent, or a cationic, anionic or nonionic surfactant in order to enhance various properties such as the dispersibility.

The mixing ratio (wt%) of the nickel zinc ferrite spherical particles to the base materials of a resin composite according to the present invention is 90 to 95/5 to 10, preferably 92 to 94/6 to 8 in consideration of the magnetic permeability and the fluidity of the ferrite resin composite.

The base material of the resin composite in the present invention is a resin with a plasticizer, lubricant, antioxidant, for example, added thereto, if necessary.

As the resin, those generally used for a resin component are usable. Examples are a thermoplastic resin such as a polystyrene resin, polyethylene resin, AS resin (acrylonitrile-styrene copolymer), ABS resin (acrylonitrile-butadiene-styrene copolymer), vinyl chloride resin, EVA resin (ethylene-vinylacetate copolymer), PMMA resin (polymethylmethacrylate), polyamide resin, polypropylene resin, EEA resin (ethylene-ethylacrylate copolymer) and PPS resin (polyphenylene sulfide), and a thermosetting resin such as a phenol resin, urea resin, melamine resin, alkyd resin, epoxy resin and polyurethane resin.

Although the ferrite resin composite of the present invention is usable both for compression molding and for injection molding, since the fluidity thereof is excellent, it is preferably used for injection molding.

The nickel zinc ferrite spherical particles of the present invention are suitable as ferrite particles for a bonded magnetic core.

The ferrite resin composite of the present invention has a large magnetic permeability of not less than 25 due to the large magnetic permeability of the ferrite particles which are mixed with the base material of a resin composite, and an excellent fluidity due to the ferrite particles having appropriate sizes and smooth spherical surfaces. The ferrite resin composite of the present invention is therefore suitable as a ferrite resin composite which is now demanded.

In addition, application of the ferrite resin composite of the present invention, which has a large magnetic permeability, to an electromagnetic wave absorber and an electromagnetic wave insulator is expected.

### Examples

The present invention is non further described in the following Examples.

In the following Examples and Comparative Examples, a cylindrical molded product having an outer diameter of 36 mm, an inner diameter of 24 mm and a height of 10 mm was produced by press-molding of granules of a mixture of ferrite particles and polyvinyl alcohol (MÄBOZÖRU T-30 produced by Matsumoto Yushi Seiyaku Co., Ltd.) under a pressure of 1 ton/cm<sup>2</sup> as a sample being measured. The magnetic permeabilities of the ferrite particles are expressed by the values obtained by measuring the magnetic permeability of the thus-obtained molded product which has been wound with a winding of 40 turns, by an impedance analyzer 4194A (produced by Yokokawa Hewlet Packard, Ltd.) at a frequency of 1 MHz.

The magnetic permeability of the ferrite resin composite of the present invention was measured by the same method described above except for using a molded product having an outer diameter of 36mm, an inner diameter of 24mm and a height of 10mm, and produced by the press-molding of the granules of the ferrite resin composite.

#### Example 1

33.85 kg of iron oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), 6.10 kg of nickel oxide and 10.95 kg of zinc oxide were mixed to produce a mixed powder for producing ferrite particles which contained 50.1 mol% of Fe<sub>2</sub>O<sub>3</sub>, 18.7 mol% of NiO and 31.2 mol% of ZnO. The mixed powder was then charged into 60.5ℓ of an aqueous solution of 0.3 wt% of polycarboxylic acid ammonium salt (SN dispersant 5468: produced by Sannopco Co., Ltd.) based on the weight of the mixed powder for producing ferrite particles. The slurry concentration in the aqueous solution was 45.7 wt%. The slurry was spray-dried to obtain granules having an average particle diameter of 105μm.

The granules obtained were calcined at a temperature of 1320°C for 3 hours to obtain spherical nickel zinc ferrite particles for a bonded magnetic core.

The magnetic permeability of the ferrite particles obtained was 32.7. It was confirmed from the observation of the scanning-type electron micrograph shown in Fig. 1 that the ferrite particles were nickel zinc ferrite spherical particles which were composed of crystal grains of 12.2μm average diameter and which had an average particle diameter of 80μm and few pores.

#### Examples 2 to 6, Comparative Examples 1 to 7

Ferrite particles for a bonded magnetic core were produced in the same way as in Example 1 except for varying the composition of the mixed powder for producing ferrite particles, the kind and the amount of surfactant, the concentration of the mixed slurry for producing ferrite particles, the particle size of the granules and the calcining temperatures.

The main producing conditions and the properties of the ferrite particles for a bonded magnetic core are shown in Table 1.

In Example 3, Fe<sub>3</sub>O<sub>4</sub> was used as the iron oxide material and in Example 5, polycarboxylic acid sodium salt (Nobcosant K: produced by Sannopco Co., Ltd.) was used as the surfactant.

In Comparative Example 7, the mixed powder for producing ferrite particles was granulated into granules about 5 mm in diameter by a conventional method without spray-drying, the granules were calcined at a temperature of 1250°C, and the calcined granules were then pulverized to obtain ferrite particles for a bonded magnetic core having a particle diameter of 39µm and containing many pores.

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#### Example 7

190 g (equivalent to 94.9 wt% based on the composite) of the ferrite particles obtained in Example 1, 10 g (equivalent to 5.0 wt% based on the composite) of ethylene-vinyl acetate copolymer resin (Evaflex 250, density : 0.95 g/cc, produced by Mitsui Polychemical Co., Ltd.) and 0.2 g (equivalent to 0.1 wt% based on the composite) of zinc stearate were kneaded at 110°C for 15 minutes by a blast mill 30C-150 (produced by Toyo Seiki Co., Ltd.) to obtain a kneaded mixture.

The thus-obtained kneaded mixture was granulated into granules having an average particle diameter of about 3 mm, and press-molded at a temperature of 75°C and a pressure of 1.5 ton/cm<sup>2</sup> to obtain a cylindrical molded product having an outer diameter of 36 mm, an inner diameter of 24 mm and a height of 10 mm. Since the ferrite resin composite filled all parts of the mold including every corner, the surface of the molded product was smooth and the circumferential portions of the upper surface and the lower surface of the cylinder were formed into complete circles without any chipping and deformation.

The magnetic permeability of the molded product was 31.0

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#### Examples 8 to 11 and Comparative Examples 8 to 11

Ferrite resin composites were produced in the same way as in Example 7 except for varying the kind and the amount of ferrite particles, the kind and amount of additive and the kneading temperature and time.

The main producing conditions and the properties of the composites obtained are shown in Table 2.

Since the ferrite resin composite filled all parts of the mold including every corner, the molded product produced from the ferrite resin composite obtained in any of Examples 8 to 11 had a smooth surface and complete circular circumferential portions of the upper surface and the lower surface of the cylinder without any chipping and deformation like the molded product obtained in Example 7.

In contrast, in the molded products produced from the ferrite resin composites obtained in Comparative Examples 8 and 10, the surfaces were uneven and chipping or deformation was observed at a part of the circumferential portions of the upper surface and the lower surface of the cylinder.

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Table 1

Examples & Comparative Examples	Mixing ratio of raw materials			Amount of Surfactant (wt%)	Slurry concentration (wt%)	Average particle diameter of granules ( $\mu\text{m}$ )	Calcining temperature ( $^{\circ}\text{C}$ )	Ferrite particles for bonded magnetic core		
	$\text{Fe}_2\text{O}_3$ (mol %)	NiO (mol %)	ZnO (mol %)					Magnetic permeability	Average particle diameter of crystal grains ( $\mu\text{m}$ )	Average particle diameter ( $\mu\text{m}$ )
Example 1	50.1	18.7	31.2	0.3	45.7	105	1320	32.7	12.2	80
Example 2	50.1	18.7	31.2	0.3	45.7	120	1280	30.2	9.5	100
Example 3	50.1	18.7	31.2	0.3	45.7	99	1150	28.0	8.2	79
Example 4	50.1	18.7	31.2	0.7	52.0	170	1100	25.3	5.1	139
Example 5	52.0	17.5	30.5	0.3	50.2	115	1300	31.5	8.3	85
Example 6	48.3	14.5	37.2	0.3	41.3	46	1320	26.2	9.2	34
Comparative Example 1	50.1	18.7	31.2	0.75	58.3	250	1250	20.2	10.0	200
Comparative Example 2	50.1	18.7	31.2	0.3	30.6	18	1150	18.3	2.2	15
Comparative Example 3	49.8	18.6	31.6	0.5	43.2	53	1000	12.0	1.5	45
Comparative Example 4	49.8	18.6	31.6	0.5	43.2	89	1380	18.6	20.0	67
Comparative Example 5	43.2	23.0	33.8	0.5	43.2	97	1250	7.0	8.5	75
Comparative Example 6	60.2	27.5	12.3	0.5	43.2	102	1180	5.0	5.3	80
Comparative Example 7	49.5	18.4	32.1	—	—	—	1250	17.5	27.1	39

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Table 2

Examples & Comparative Examples	Manufacture of ferrite resin composite										Ferrite resin composite	
	Ferrite particles		Resin			Additive		Kneading		Magnetic permeability		
	Kind	Amount (wt%)	Kind	Amount (wt%)	Kind	Amount (wt%)	Temperature (°C)	Time (min.)				
Example 7	Example 1	95.0	Evaflex 250 (produced by Mitsui Polychemical Co., Ltd.)	4.9	Zn stearate	0.1	110	15	31.0			
Example 8	Example 1	93.0	ditto	7.9	Zn stearate	0.1	100	15	28.4			
Example 9	Example 2	95.0	ditto	4.9	Zn stearate	0.1	110	15	28.7			
Example 10	Example 1	92.0	12-Nylon 3014U (produced by Ube Industries, Ltd.)	7.9	Ca stearate	0.1	250	15	28.5			
Example 11	Example 5	91.0	ditto	8.9	Ca stearate	0.1	250	15	27.2			
Comparative Examples 8	Comparative Examples 1	95.0	Evaflex 250 (produced by Mitsui Polychemical Co., Ltd.)	4.9	Zn stearate	0.1	110	15	18.6			
Comparative Examples 9	Comparative Examples 2	95.0	ditto	4.9	Zn stearate	0.1	120	15	16.8			
Comparative Examples 10	Comparative Examples 3	92.0	12-Nylon 3014U (produced by Ube Industries, Ltd.)	7.9	Ca stearate	0.1	250	15	10.6			
Comparative Examples 11	Comparative Examples 7	95.0	Evaflex 250 (produced by Mitsui Polychemical Co., Ltd.)	4.9	Zn stearate	0.1	120	15	16.5			

**Claims**

- 5 1. Spherical ferrite particles suitable for a bonded magnetic core, which particles comprise uniform crystal grains of from 5 to 15  $\mu\text{m}$  in average diameter and have an average particle diameter of from 20 to 150  $\mu\text{m}$  and a magnetic permeability of not less than 25;  
the above magnetic permeability being the magnetic permeability of a molded product obtained by:
- 10 a) press-molding the particles and polyvinyl alcohol under a pressure of 1 ton/cm<sup>2</sup> to form a cylindrical molded product having an outer diameter of 36mm, an inner diameter of 24mm and a height of 10mm; and  
b) winding the molded product with a winding of 40 turns and measuring the magnetic permeability thereof with an impedance analyzer at a frequency of 1 MHz.
- 15 2. Ferrite particles according to claim 1, which comprise from 48 to 53 mol% of Fe<sub>2</sub>O<sub>3</sub>, from 13 to 20 mol% of NiO and from 27 to 39 mol% of ZnO.
- 20 3. A ferrite resin composite comprising ferrite particles according to claim 1 or 2 and a base resin, said ferrite resin composite having a magnetic permeability of not less than 25;  
the above magnetic permeability being determined by:
- a) press-molding granules of said ferrite resin composite under a pressure of 1 ton/cm<sup>2</sup> to form a cylindrical molded product having an outer diameter of 36mm, an inner diameter of 24mm and a height of 10mm; and  
25 b) winding the molded product with a winding of 40 turns and measuring the magnetic permeability thereof with an impedance analyzer at a frequency of 1 Mhz.
4. A composite according to claim 3, which comprises from 92 to 94 wt% of the particles and from 8 to 6 wt% of the base resin.
- 30 5. A composite according to claim 3 or 4 in the form of a magnetic core.
6. A process for producing ferrite particles as defined in claim 1 or 2 which comprises:
- (i) mixing a) from 47 to 55 mol%, calculated as Fe<sub>2</sub>O<sub>3</sub>, of an iron oxide or iron oxide hydroxide powder,  
35 b) from 10 to 23 mol%, calculated as NiO, of a nickel oxide powder and c) from 25 to 40 mol%, calculated as ZnO, of a zinc oxide powder and d) water containing from 0.2 to 1.0 wt% of a surfactant based on the total weight of the powders a), b) and c) so as to prepare a slurry having a slurry concentration of from 40 to 60 wt%,  
(ii) spray-drying the resultant slurry so as to obtain spherical granules having an average particle diameter of from 25 to 180  $\mu\text{m}$ , and  
40 (iii) calcining the obtained granules at a temperature of from 1100 to 1350°C.
7. A process according to claim 6 in which stage (i) comprises mixing:
- a) from 48 to 53 mol% of Fe<sub>2</sub>O<sub>3</sub>  
b) from 13 to 20 mol% of NiO  
45 c) from 27 to 39 mol% of ZnO  
d) water containing from 0.2 to 0.8 wt% of a surfactant.
8. A process according to claim 6 or 7 in which the surfactant in stage (i) is an alkali metal salt, an amine salt, an ammonium salt of an anionic surfactant, a fatty acid salt or a hydrochloride of a cationic surfactant.
- 50 9. A process according to any one of claims 6 to 8 which comprises the additional step of kneading the ferrite particles with the base resin and press molding the mixture to produce a moulded product.

55 **Patentansprüche**

1. Kugelförmige, für einen Verbundmagnetkern geeignete Ferriteilchen, wobei die Teilchen einheitliche Kristallkörner mit einem Durchschnittsdurchmesser von 5 bis 15  $\mu\text{m}$  umfassen und einen Durchschnittsteil-

chendurchmesser von 20 bis 150 µm und eine nicht geringere magnetische Permeabilität als 25 aufweisen; wobei die zuvor genannte magnetische Permeabilität die magnetische Permeabilität eines Formproduktes ist, welches erhalten wurde durch:

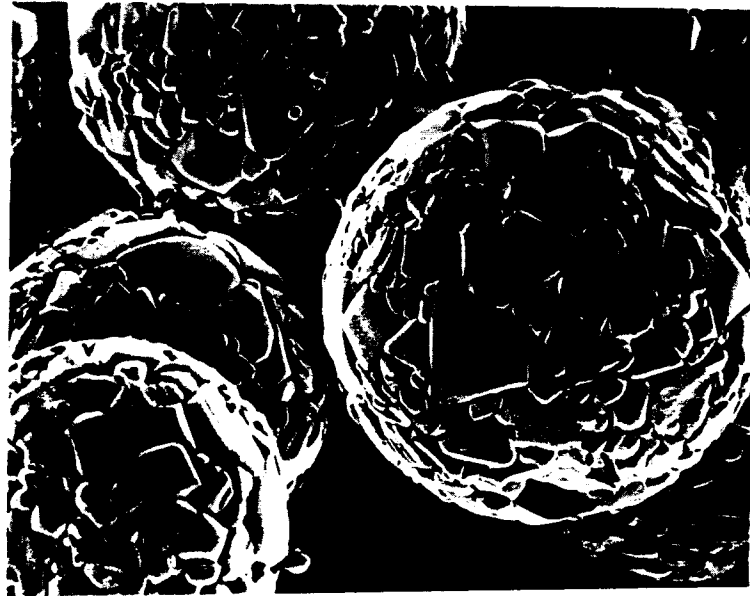
- 5 a) Preßformen der Teilchen und Polyvinylalkohol bei einem Druck von 1 t/cm<sup>2</sup> unter Bildung eines zylindrischen Formproduktes mit einem Außendurchmesser von 36 mm, einem Innendurchmesser von 24 mm und einer Höhe von 10 mm; und
- b) Aufwickeln des Formproduktes mit einer Wickelung von 40 Windungen und Messen dessen magnetischer Permeabilität mit einem Impedanzanalysator bei einer Frequenz von 1 MHz.
- 10 2. Ferritteilchen nach Anspruch 1, umfassend 48 bis 53 Mol.% Fe<sub>2</sub>O<sub>3</sub>, 13 bis 20 Mol.% NiO und 27 bis 39 Mol.% ZnO.
3. Ferritharzcomposit, umfassend Ferritteilchen nach Anspruch 1 oder 2 und ein Grundharz, wobei das Ferritharzcomposit eine nicht geringere magnetische Permeabilität als 25 aufweist; wobei die zuvor genannte magnetische Permeabilität bestimmt worden ist durch
  - 15 a) Preßformen der Granalien des Ferritharzcomposits bei einem Druck von 1 t/cm<sup>2</sup> unter Bildung eines zylindrischen Formproduktes mit einem Außendurchmesser von 36 mm, einem Innendurchmesser von 24 mm und einer Höhe von 10 mm; und
  - b) Aufwickeln des Formproduktes mit einer Wickelung von 40 Windungen und Messen dessen magnetischer Permeabilität, mit einem Impedanzanalysator bei einer Frequenz von 1 MHz.
- 20 4. Composit nach Anspruch 3, umfassend 92 bis 94 Gew.% der Teilchen und 8 bis 6 Gew.% des Grundharzes.
5. Composit nach Anspruch 3 oder 4 in Form eines magnetischen Kerns.
- 25 6. Verfahren zum Herstellen von Ferritteilchen nach Anspruch 1 oder 2, umfassend:
  - (i) Mischen von
    - 30 a) 47 bis 55 Mol.%, berechnet als Fe<sub>2</sub>O<sub>3</sub>, eines Eisenoxid- oder Eisenoxidhydroxidpulvers,
    - b) 10 bis 23 Mol.%, berechnet als NiO, eines Nickeloxidpulvers und
    - c) 25 bis 40 Mol.%, berechnet als ZnO, eines Zinkoxidpulvers und
    - d) Wasser, welches 0,2 bis 1,0 Gew.% eines oberflächenaktiven Mittels, bezogen auf das Gesamtgewicht der Pulver a), b) und c) enthält, wobei eine Aufschlammung mit einer Aufschlammungskonzentration von 40 bis 60 Gew.% hergestellt wird,
  - 35 (ii) Sprühtrocknen der sich ergebenden Aufschlammung, wobei kugelförmige Granalien mit einem Durchschnittsteilchendurchmesser von 25 bis 180 µm erhalten werden, und
  - (iii) Kalzinieren der erhaltenen Granalien bei einer Temperatur von 1.100 bis 1.350°C.
7. Verfahren nach Anspruch 6, wobei die Stufe (i) Mischen von
  - 40 (a) 48 bis 53 Mol.% Fe<sub>2</sub>O<sub>3</sub>,
  - (b) 13 bis 20 Mol.% NiO,
  - (c) 27 bis 39 Mol. % ZnO,
  - (d) Wasser, welches 0,2 bis 0,8 Gew.% eines oberflächenaktiven Mittels enthält, umfaßt.
8. Verfahren nach Anspruch 6 oder 7, wobei das oberflächenaktive Mittel in Stufe (i) ein Alkalimetallsalz, ein Ammoniumsalz, ein Ammoniumsalz eines anionischen oberflächenaktiven Mittels, ein Fettsäuresalz oder ein Hydrochlorid eines kationischen oberflächenaktiven Mittels ist.
- 45 9. Verfahren nach einem der Ansprüche 6 bis 8, umfassend die zusätzliche Stufe des Knetens der Ferritteilchen mit dem Grundharz und Preßformen der Mischung unter Herstellung eines Formproduktes.

## Revendications

- 55 1. Particules de ferrite sphériques utilisables pour un noyau magnétique aggloméré, ces particules comprenant des grains cristallins uniformes de 5 à 15 µm de diamètre moyen et ayant un diamètre moyen de particule de 20 à 150 µm et une perméabilité magnétique non inférieure à 25 ;  
la perméabilité magnétique ci-dessus étant la perméabilité magnétique d'un produit moulé obtenu par :

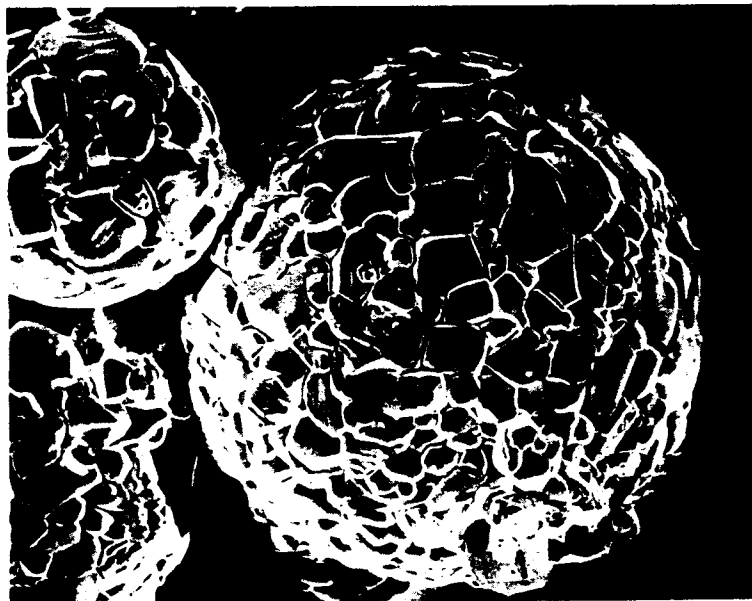
- a) moulage par compression des particules et d'alcool polyvinylique sous une pression d'une tonne/cm<sup>2</sup> pour former un produit moulé cylindrique ayant un diamètre externe de 36 mm, un diamètre interne de 24 mm et une hauteur de 10 mm ; et
- b) formation autour du produit moulé d'un enroulement de 40 tours et mesure de la perméabilité magnétique de celui-ci avec un analyseur d'impédance à une fréquence de 1 MHz.
- 5
2. Particules de ferrite selon la revendication 1, qui comprennent de 48 à 53 moles % de Fe<sub>2</sub>O<sub>3</sub>, de 13 à 20 moles % de NiO et de 27 à 39 moles % de ZnO.
- 10
3. Composite ferrite-résine comprenant des particules de ferrite selon les revendications 1 ou 2 et une résine de base, ce composite ferrite-résine ayant une perméabilité magnétique non inférieure à 25 ;  
la perméabilité magnétique ci-dessus étant déterminée par :
- a) moulage par compression de granulés de ce composite ferrite-résine sous une pression d'une tonne/cm<sup>2</sup> pour former un produit moulé cylindrique ayant un diamètre externe de 36 mm, un diamètre interne de 24 mm et une hauteur de 10 mm ; et
- 15
- b) formation autour du produit moulé d'un enroulement de 40 tours et mesure de la perméabilité magnétique de celui-ci avec un analyseur d'impédance à une fréquence de 1 MHz.
4. Composite selon la revendication 3, qui comprend de 92 à 94 % en poids des particules et de 8 à 6 % en poids de la résine de base.
- 20
5. Composite selon les revendications 3 ou 4 sous la forme d'un noyau magnétique.
6. Procédé de préparation de particules de ferrite selon les revendications 1 ou 2, qui comprend :
- 25
- (i) le mélange a) de 47 à 55 moles %, calculées en Fe<sub>2</sub>O<sub>3</sub>, d'une poudre d'oxyde de fer ou d'hydroxyde de fer, b) de 10 à 23 moles %, calculées en NiO, d'une poudre d'oxyde de nickel et c) de 25 à 40 moles %, calculées en ZnO, d'une poudre d'oxyde de zinc et d) de l'eau contenant de 0,2 à 1,0 % en poids d'un agent tensioactif par rapport au poids total des poudres a), b) et c), de manière à préparer une bouillie ayant une concentration de 40 à 60 % en poids
- 30
- (ii) séchage par pulvérisation de la bouillie obtenue de manière à obtenir des granulés sphériques ayant un diamètre moyen de particule de 25 à 180 μm et
- (iii) calcination des granulés obtenus à une température de 1100 à 1350 °C.
7. Procédé selon la revendication 6, dans lequel le stade (i) comprend le mélange :
- 35
- a) de 48 à 53 moles % de Fe<sub>2</sub>O<sub>3</sub>  
b) de 13 à 20 moles % de NiO  
c) de 27 à 39 moles % de ZnO  
d) d'eau contenant 0,2 à 0,8 % en poids d'un agent tensioactif.
8. Procédé selon les revendications 6 ou 7, dans lequel l'agent tensioactif du stade (i) est un sel de métal alcalin, un sel d'amine, un sel d'ammonium d'un agent tensioactif anionique, un sel d'acide gras ou un chlorhydrate d'un agent tensioactif cationique.
- 40
9. Procédé selon l'une quelconque des revendications 6 à 8, qui comprend le stade supplémentaire de malaxage de particules de ferrite avec la résine de base et de moulage par compression du mélange pour former un produit moulé.
- 45
- 50
- 55

*Fig. 1*



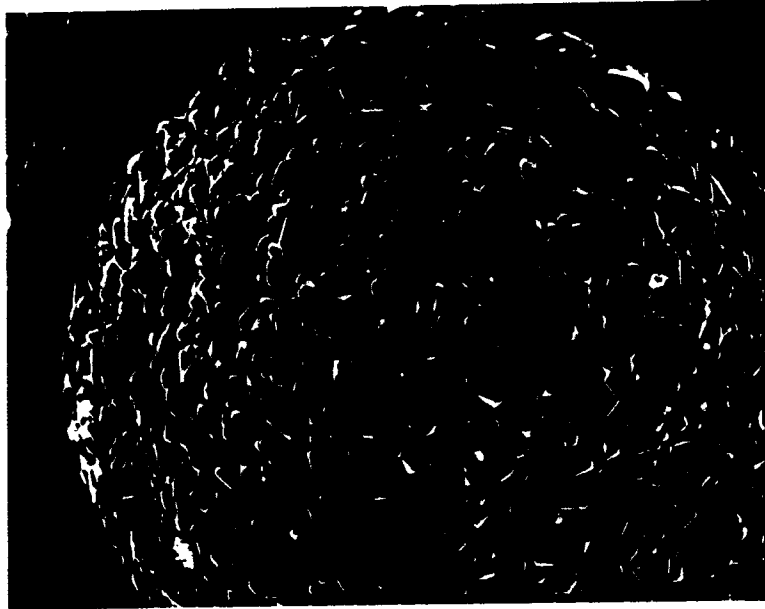
(x6500)

*Fig. 2*



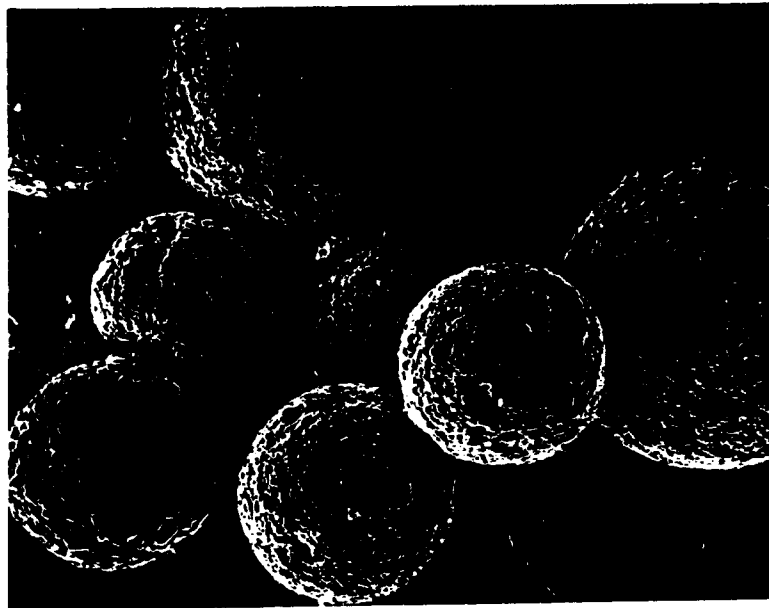
(x6500)

*Fig. 3*



(x6500)

*Fig. 4*



(x6500)

*Fig. 5*



(x6500)

*Fig. 6*



(x6500)