Feb. 2, 1965 E. MOSER ETAL 3,168,476
PROCESS FOR PRODUCING MAGNETIC MANGANESE-ZINC FERRITE WITH ISOPERM CHARACTER
Filed Feb. 3, 1961 3 Sheets-Sheet 1

Fig.1

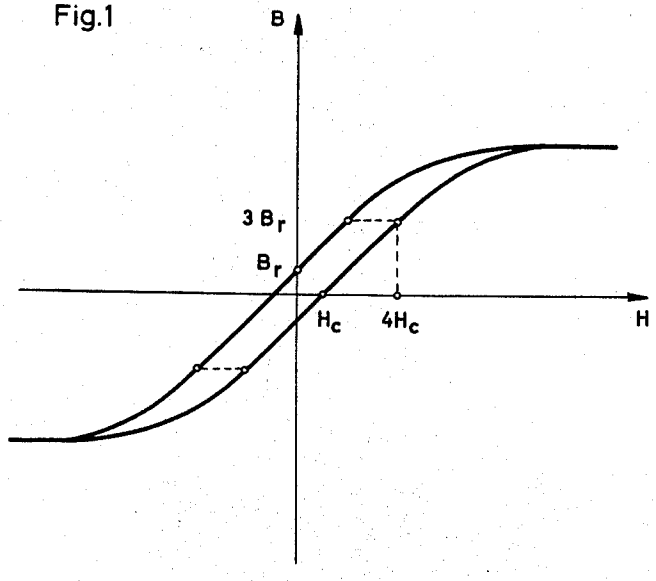


Fig.3

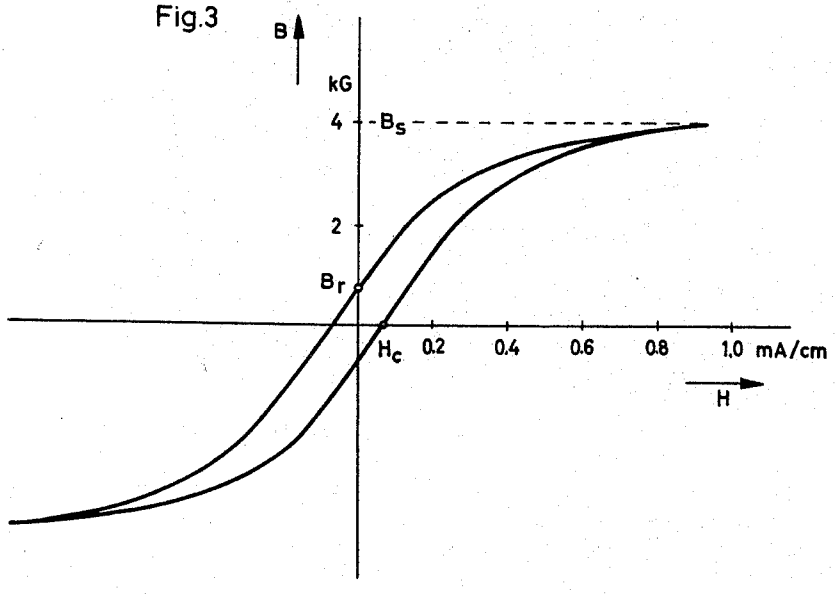
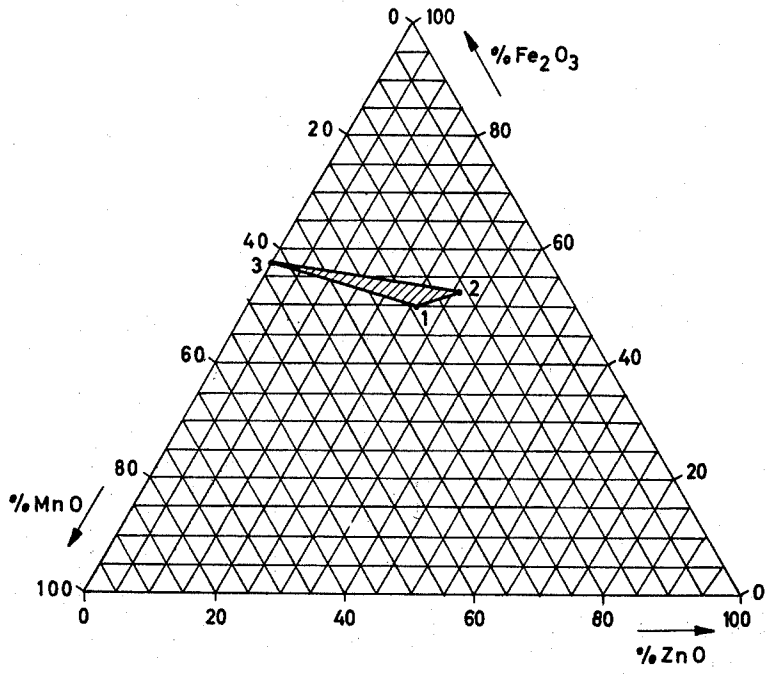


Fig. 2


0
100
% Fe2 O3
20
80
40
60
3
2
1
60
40
80
20
% Mn O
100
0
0
20
40
60
80
100
% Zn O

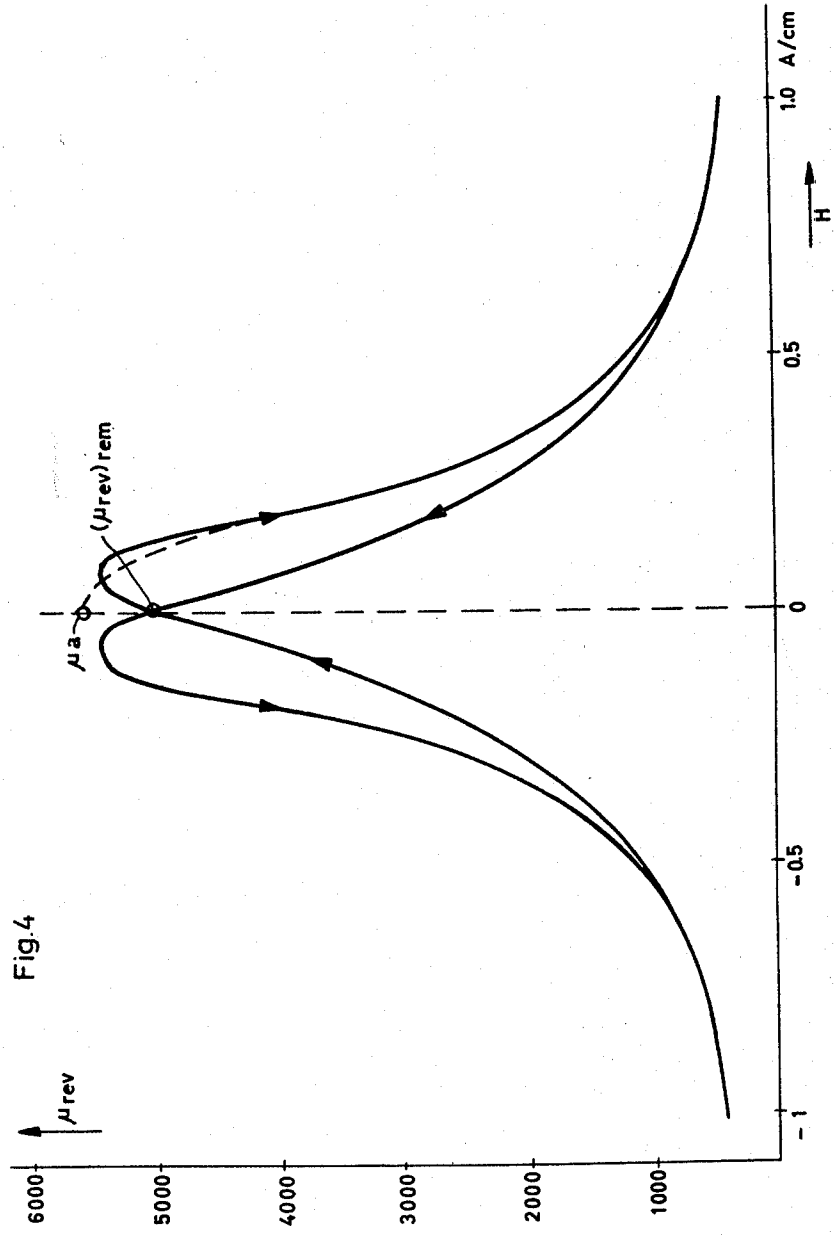

1.0 A/cm
H
0.5
0
-0.5
-1
$(\mu_{rev})_{rem}$
μ_a
μ_{rev}
6000
5000
4000
3000
2000
1000

Fig.4

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3,168,476

PROCESS FOR PRODUCING MAGNETIC MANGANESE-ZINC FERRITE WITH ISOPERM CHARACTER

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8 Claims. (Cl. 252—62.5)

This invention is concerned with a method of producing a soft magnetic ferrite with isoperm character.

The isoperm character is realized in connection with magnetic materials the hysteresis loop of which has, in addition to a relatively low remanence induction and coercive power, as far reaching as possible a linear parallelism of the inclined branches of the hysteresis loop. The term "isoperm character" is intended to mean that the hysteresis loop is in its middle part described by an obliquely extending parallelogram the width of which corresponds to twice the coercive power H_c and the height of which corresponds at least to twice the remanence induction B_r. The remanence induction shall amount to less than about 25 percent of the saturation induction B_s.

The properties of such isoperm magnetic materials are for many instances of use extraordinarily advantageous. Such magnetic materials offer as compared with magnetic materials with normal hysteresis loop great advantages, particularly as core materials for highgrade filter coils.

The isoperm ferrites according to the invention show, in addition to the general advantages of ferrites so far as eddy current losses and high initial permeability are concerned, low remanence and with increasing field strength only slight increase of permeability up to maximum permeability. The hysteresis losses are moreover very low. The alignment error of the reversible permeability is likewise slight. Moreover, the initial permeability is with ferrites according to the invention very constant as to time and relatively insensitive to temporary magnetic or thermal loads.

The ferrites produced according to the invention are very densely sintered, so that the isoperm-like hysteresis loop obviously cannot be traced to a shearing of the ferrite which would produce unfavorable and, of course, undesired properties. The ferrites according to the invention do not require any treatment in a magnetic field.

There are ferrites known with an isoperm loop, which are produced by particular magnetic field treatment from socalled Perminvar ferrites. The isoperm character of these ferrites is effected by particular anisotropic effects. They have only an initial permeability up to about 120.

The method according to the invention proposes to produce isoperm ferrites based upon iron-manganese-zinc, utilizing initial substances, for example, metal oxides or metal compounds, which are so pure that the ferrite does not contain more than about 0.2 percent by weight of total impurities and of these, at the most about 0.03 percent by weight silicic acid and at the most respectively about 0.03 percent by weight of other disturbing substances, wherein the amounts of the ferrite-forming initial substances are determined by a mixing area in the three substance iron-manganese-zinc diagram, such mixing area being described by the corner points, namely

(1) 50 mole percent Fe_2O_3,
24 mole percent MnO,
26 mole percent ZnO;
(2) 52 mole percent Fe_2O_3,
16 mole percent MnO,
32 mole percent ZnO; and

(3) 57.5 mole percent Fe_2O_3,
42.5 mole percent MnO.

These initial substances are intermixed and preferably annealed prior to the final sintering thereof. The sintered ferrite body is cooled in an inert gas atmosphere, for example, in nitrogen.

Disturbing substances are particularly those elements the ion radii of which are greater than the ion radius of the largest element partaking in the building up of the ferrite grid, in the present case, the manganese.

Of particular interest in the range of the three substance diagram determined by the invention is the region with less than 24 mole percent MnO. Particularly high initial permeabilities up to $\mu_a=7000$ can be reached in this region. The region with less than 10 mole percent ZnO is distinguished by high Curie temperatures (T_c) above 250° C. and high values of the saturation magnetization in the produced ferrite which are only slightly dependent upon the temperature.

The oxides composed according to the invention from the region of the three substance diagram are mixed wet for about six hours, for example in a rocker mill, thereupon dried and preannealed at a temperature between 850° C. and 950° C., preferably at 900° C., and thereafter again subjected to wet grinding for about two hours. Cores are now formed from the resulting powder by pressure molding and such cores are sintered in air, nitrogen or an air-nitrogen mixture or first in air and thereafter in nitrogen, at temperatures between 1240° C. and 1350° C. for one to fifteen hours, preferably for two hours, whereupon they are cooled in an inert gas atmosphere, for example, in pure nitrogen. In accordance with the invention, the formation of the isoperm character is favored by rapid cooling from the sinter temperature to a temperature from 900° C. to 500° C. within an interval from five to fifteen minutes. Such rapid cooling is particularly indicated in the case of cores the dimensions of which are at least in one direction very small, for example ring cores with a thickness of only one millimeter or less.

The ferrites produced according to the invention have initial permeabilities from about $\mu_a=2000$ to 7000, relative temporal inconstancy values $-i_z/\mu_a$ smaller than 5.10^{-6} and incidental reference hysteresis value h/u^2_a smaller than $0.5.10^{-3}$ cm./ka.; wherein h is Jordan's incidental hysteresis value (see, for example, M. Kornetzki, Zeitschrift für angewandte Physik, 4 (1952), pages 343 to 345 and 6 (1954), pages 547 to 550), and i_z being the relative variation of the initial permeability in the time interval from one to ten hour after passing temperature increase to 150° C. The reversible permeability at the remanence point lies about 10 percent below the initial permeability. The density of the cores amounts to about 4.6 to 4.8 g./cm.^{3}. The isoperm character is less pronounced when the cores are produced without the preannealing of the oxide mixture.

Some examples will now be given concerning the production of isoperm ferrites according to the invention.

Example 1

Composition:
53.5 mole percent Fe_2O_3,
30.5 mole percent MnO, and
16.0 mole percent ZnO.

The oxides which are constituted so that the total impurities in the end product amount to less than 0.2 percent by weight, are with the addition of water in an amount of three times that of the oxides, intermixed by treatment in a suitable mill, for example, a rocker mill, lasting for about six hours, and preannealed at 900° C. for one hour. The preannealed powder is ground fur-

ther with an addition of a binder agent, for two hours, whereupon rings are pressure molded therefrom which are sintered for one hour in nitrogen at 1280° C. The rings have an outer diameter of 20 millimeters and a thickness of 6 millimeters. The cooling from the sinter temperature to normal temperature is effected within twelve hours in pure nitrogen with an oxygen content of less than 0.02 percent by volume. The ferrites exhibited the following characteristic magnetic values:

μ_a=3600; h/μ^2_a=0.15.10^{-3} cm./ka. at 20 cycles
$-i_z/\mu_a$=3.5.10^{-6}; T_c=190° C.; $\mu_{max.}/\mu_a$=1.25
B_s=4.4 kg.; B_r/B_s=0.16

wherein $\mu_{max.}$=maximum permeability, B_s=magnetization at 10 a./cm., B_r=remanent magnetization.

Example 2

Composition:
52.4 mole percent Fe_2O_3,
25.4 mole percent MnO, and
22.2 percent mole ZnO.

Cores formed as described in the first example, are sintered at 1320° C. for two hours in nitrogen containing 7 percent by volume oxygen, and thereupon rapidly cooled to 850° C., within ten minutes, in nitrogen containing 0.2 percent by volume oxygen. The further cooling to room temperature is effected within six hours in nitrogen with 0.2 percent O_2. There resulted the following values:

μ_a=3900; h/μ^2_a=0.3.10^{-3} cm./ka. at 20 cycles
$-i_z/\mu_a$=2.5.10^{-6}; T_c=130° C.; $(\mu_{rev})_{rem/\mu a}$=0.915
B_r/B_s=0.16

Example 3

Composition:
53.5 mole percent Fe_2O_3,
30.5 mole percent MnO, and
16.0 mole percent ZnO.

Ring cores which were again formed as described in the first example, had a thickness of only one millimeter and a cross sectional area of about one square millimeter. They were sintered for one hour in air at 1240° C., thereafter for one hour in nitrogen, and thereupon cooled to 500° C. in pure nitrogen within five minutes. The further cooling to room temperature was effected within about four hours, likewise in nitrogen. The ferrites produced in this manner gave the following measured values:

μ_a=5600; h/μ^2_a=0.2.10^{-3} cm./ka. at 20 cycles
$-i_z/\mu_a$=1.0.10^{-6}; T_c=190 C.; $(\mu_{rev})_{rem/\mu a}$=0.87

wherein $(\mu_{rev})_{rem}$=reversible permeability in the remanence point.

Example 4

Composition:
55.5 mole percent Fe_2O_3,
36.5 mole percent MnO, and
8.0 mole percent ZnO.

Cores produced in the manner described in connection with the first example exhibited the following characteristic magnetic values:

μ_a=2450; h/μ^2_a=0.5.10^{-3} cm./ka.
T_c=300° C.; B_s=5.3 ka. (at 25 oe.); B_r/B_s=0.22

Example 5

Composition:
52.5 mole percent Fe_2O_3,
23.5 mole percent MnO, and
24.0 mole percent ZnO.

The iron oxide used in this example had a tetra thread-like particle structure. The initial raw materials are constituted so that the end product contains substantially only the impurities noted in percent by weight, namely, 0.02 percent SiO_2; 0.02 percent TiO_2; 0.002 percent Al_2O_3; 0.02 percent CaO. Cores produced as described in the first example are sintered at 1270° C. first for three hours

in air and thereafter for twelve hours in nitrogen with an oxygen content of less than 0.02 volume percent, whereupon they are slowly cooled to room temperature, within about ten hours, in nitrogen. The following values were measured:

μ_a=7000; h/μ^2_a=0.2.10^{-3} cm./ka.
T_c=110° C.; B_r/B_s=0.24

Further explanations are rendered below with reference to the accompanying drawings.

FIG. 1 shows the hysteresis loop of a magnetic material with isoperm structure;

FIG. 2 represents the three substance diagram

Fe_2O_3—MnO—ZnO

with the area or region according to the invention;

FIG. 3 shows the hysteresis loop of an isoperm ferrite made according to Example 1; and

FIG. 4 shows the course of the reversible permeability of an isoperm ferrite made according to Example 3, in dependence upon the field strength.

It will be seen from FIG. 1 that the central region of both hysteresis loop legs, in a hysteresis loop of a magnetic material with isoperm structure, rises linearly, describing due to its parallelism a parallelogram with a width corresponding to twice the coercive power, the height of the parallelogram corresponding in this case to six times the remanence induction.

The three-substance diagram Fe_2O_3—MnO—ZnO, represented in FIG. 2 shows the area provided by the present invention which contains the quantitative composition of the initial oxides employed in the new method. Numerals 1, 2 and 3 indicate the corner points for which numerical values are specified in the claims.

In the hysteresis loop of an isoperm ferrite produced according to the Example 1, as shown in FIG. 3, the remanence induction B_r lies at about 0.75K gauss and the coercive power H_c at about 0.07 ma./cm.

In FIG. 4, showing the course of the reversible permeability of an isoperm ferrite made according to the Example 3 in dependence upon the field strength, the dash line indicates the course of the reversible permeability extending from the curve which denotes the demagnetized condition. Also apparent from this figure is the slight error or alignment of the reversible permeability between effective magnetization and demagnetization.

Changes may be made within the scope and spirit of the appended claims which define what is believed to be new and desired to have protected by Letters Patent.

We claim:

1. A method of producing a soft magnetic ferrite with isoperm character upon a basis of iron-manganese-zinc, with an initial permeability of $\mu_a \geqq 2000$ and a ratio of the remanence induction B_r to saturation induction B_s of

$$\frac{B_r}{B_s} < 0.25$$

which does not contain more than a total of about 0.2% by weight of foreign substances, including at the most about 0.03% by weight silicic acid and at the most about 0.03% by weight of any other disturbing foreign substance, the initial substances being intermixed in proportions of mole percentages in a range with the following corner points in a three substance diagram:

(1) 50 mole percent Fe_2O_3
24 mole percent MnO
26 mole percent ZnO
(2) 52 mole percent Fe_2O_3
16 mole percent MnO
32 mole percent ZnO
(3) 57.5 mole percent Fe_2O_3
42.5 mole percent MnO.

comprising the steps of annealing the mixture at temperatures between about 850 and 950° C., thereafter grinding

the annealed material, molding to the desired shape, sintering the molded material at temperatures between 1200° C. and 1350° C., and cooling the same in an inert gas atmosphere containing less than about 0.02 volume percent oxygen.

2. A method of producing a soft magnetic ferrite with isoperm character on the basis of iron-manganese-zinc, according to claim 1, comprising the steps, following sintering of the molded material, of initially quickly cooling the same within about 5 to 15 minutes, from the sinter temperature to a temperature between 900° C. and 500° C., in an inert gas atmosphere containing less than 0.5 volume percent oxygen, and thereafter gradually cooling it to room temperature.

3. A method according to claim 1, wherein the final cooling is slowly effected within 12 to 20 hours.

4. A method according to claim 3, wherein the initial substances are intermixed in wet condition.

5. A method according to claim 1, wherein the annealing is effected within a short time of about one hour, at about 900° C.

6. A method according to claim 2, wherein the sintering is effected at temperatures between 1240° C. and 1320° C., within 1 to 15 hours, in an atmosphere selected from the group of air and nitrogen.

7. A method according to claim 2, wherein the molded material is sintered at temperatures between 1200° C. and 1300° C., first for about 3 to 5 hours in air, and thereupon for about 3 to 12 hours in pure nitrogen.

8. A method according to claim 2, wherein the sinter temperature and the sinter duration are so selected, that the density of the ferrite material amounts to more than 4.5 g./cm.^{3}.

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