June 20, 1961 O. ECKERT 2,989,478

FERRITE WITH CONSTRICTED MAGNETIC HYSTERESIS LOOP

Filed Nov. 15, 1956 2 Sheets-Sheet 1

FIG. 1a

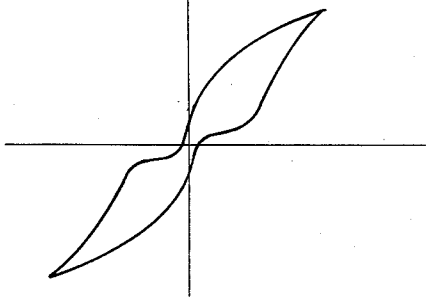


FIG. 1b

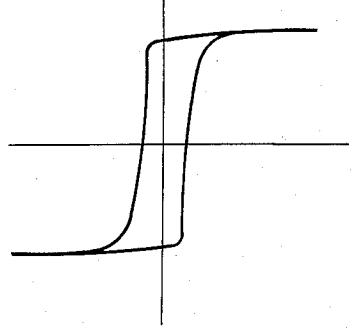
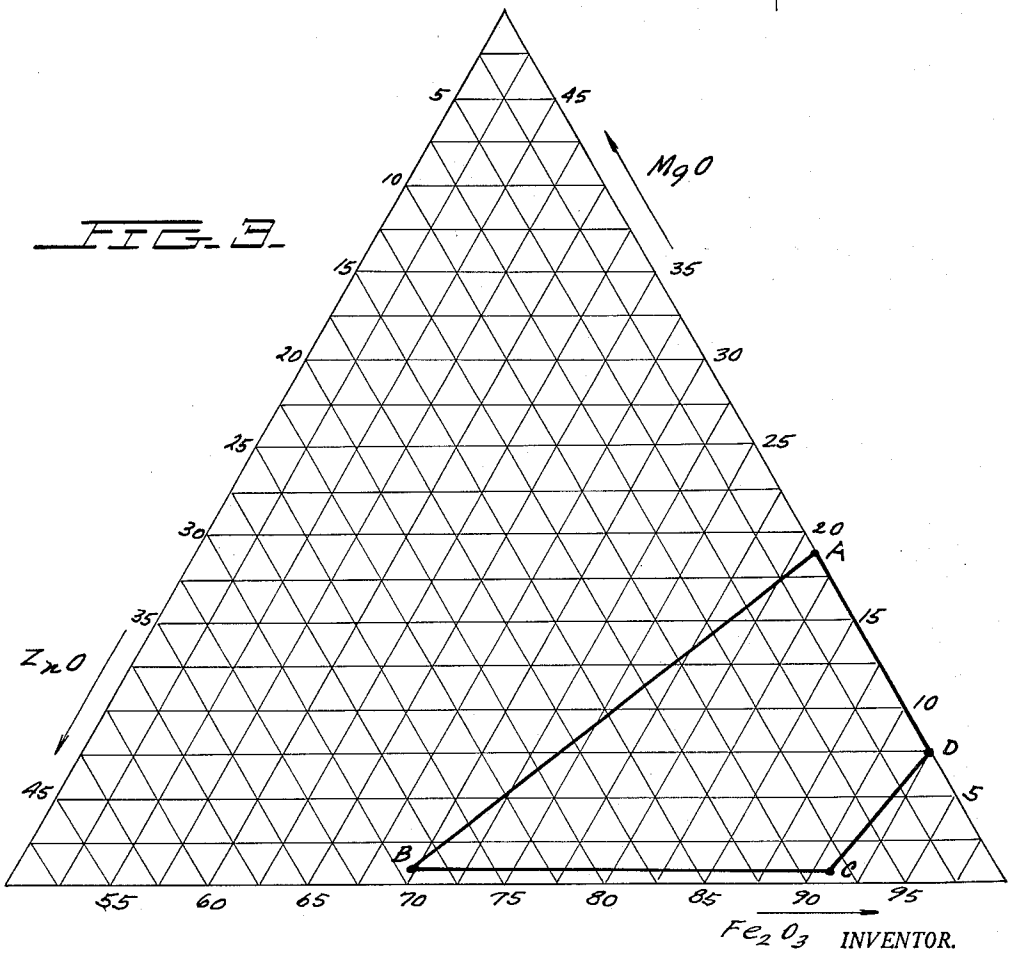


FIG. 3



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FIG. 2a.

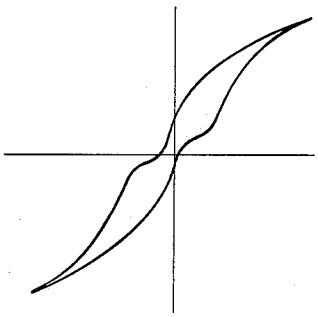


FIG. 2b.

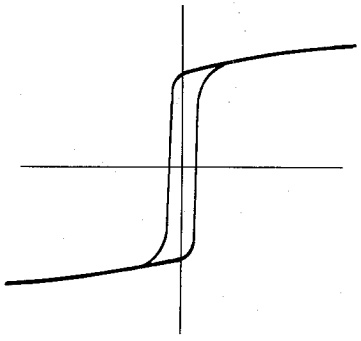
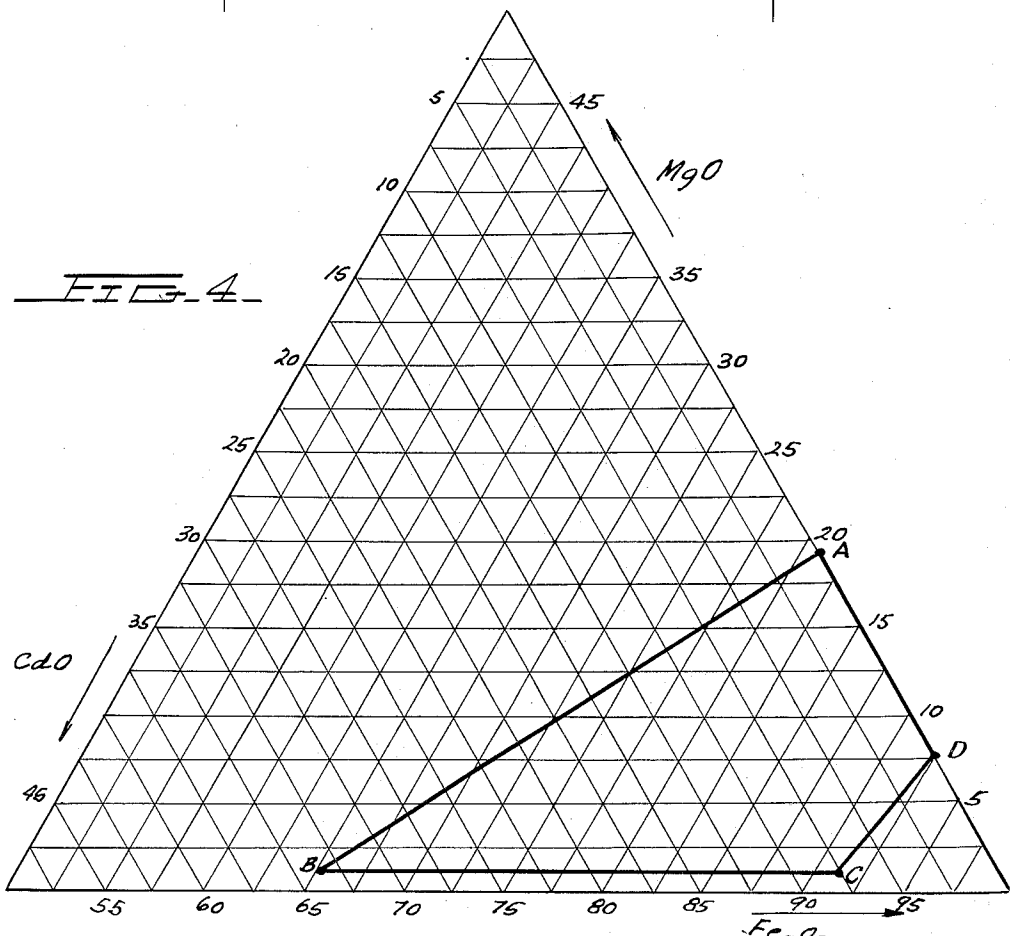


FIG. 4.



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FERRITE WITH CONSTRICTED MAGNETIC HYSTERESIS LOOP

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5 Claims. (Cl. 252—62.5)

Ferromagnetic metals with constricted hysteresis loops (see, for example, Bozorth, "Ferromagnetism," published by Nostrand Co., Inc., 1951, pages 498 to 499), have, as is well known, at small field strength within the constriction area, constant permeability, i.e., permeability independent of the field strength equal to the initial permeability, very low hysteresis losses and, in general, small residual losses. As indicated in the above cited literature, such materials may be subjected to thermo-magnetic treatment. By thermomagnetic treatment, in this connection, is meant the passing through a thermic cycle during the simultaneous presence of a magnetic longitudinal or transverse field. The concept of longitudinal or transverse field is, in this connection, to be understood as relative to the later measuring field; a longitudinal or transverse field, respectively, means that such field, during the thermomagnetic treatment, is parallel, respectively vertical, to the later measuring field. Through this type of treatment, these ferromagnetic materials display a substantial alteration of the form of the hysteresis loop, and hence a change of the magnetic properties.

This invention is based on the discovery that it is possible to make specific ferrites showing a constricted magnetic hysteresis loop which are, consequently, capable of thermomagnetic treatment similarly as for metals.

The invention teaches the production of such ferrites of the magnesium-zinc or magnesium-cadmium ferrite system which can be subjected to thermomagnetic treatment of the above type, and are distinguished from hitherto familiar ferrites by the fact that, under the same manufacturing conditions, they have constricted hysteresis loops.

In accordance with the invention, ferrites with this characteristic in the Mg-Zn or Mg-Cd ferrite must have a composition of at least 50 mol percent Fe_2O_3, and a small addition of cobalt oxide. The addition of cobalt oxide is suitably determined between 0.1 and 5% by weight, calculated on the total basic batch of the Mg-Zn or Mg-Cd ferrite, expressed in metallic oxides. The invention has shown that it is particularly advantageous to choose the cobalt oxide content between 0.35 and 1.5 by weight, calculated on the basic batch. The Mg-Zn or Mg-Cd ferrites in question, which react strongly to the addition of cobalt oxide with a constricted loop, cover, in the three-component system Fe_2O_3-MgO-ZnO or Fe_2O_3-MgO-CdO the area defined in the attached diagrams (FIGS. 3 and 4) by the quadrangle A, B, C, D. The compositions at the corners in percent by weight are:

(*a*) for the Fe_2O_3-MgO-ZnO system:

	Fe_2O_3	MgO	ZnO
A	81	19	0
B	70	1	29
C	91	1	8
D	92.5	7.5	0

(*b*) for the Fe_2O_3-MgO-CdO system:

	Fe_2O_3	MgO	CdO
A	81	19	0
B	65	1	34
C	91	1	8
D	92.5	7.5	0

The above ferrites may be prepared in the usual way, either by joint or partial precipitation, from corresponding metal salt solutions, or, as is customary in ceramic arts, they may be prepared for further processing by wet milling and mixing of the respective metal oxides. The powdered mixtures thus obtained, after drying, may be given the desired form either immediately by dry pressing, extruding, or similar methods, or it may be desirable, before ceramic forming, to proceed with a calcining firing of the entire composition or only a part thereof preferably between 750° and 1100° C. for the Mg-Zn-ferrite system or 750° C. to 1250° C. for the Mg-Cd-ferrite system. The thus manufactured parts are sintered, depending on the composition, in a suitable way between 1180° C. and 1350° C. for the Mg-Zn-ferrite system or 1250° C. and 1400° C. for the Mg-Cd-ferrite system. To produce the constricted hysteresis loop in ferrites, in accordance with the invention, it is necessary that the cooling takes place slowly, particularly in the temperature range between 700° C. and room temperature. The cooling speed is dependent upon the volume of the fired body. As a criterion, it may be stated that for a ring of about 46 mm. outside diameter, 34 mm. inside diameter, and 10 mm. height, the cooling time from 700° C. to room temperature should take not less than 12 hours. If the rings are cooled rapidly, the effect of loop construction does not occur. However, the constriction may be regained even for rings cooled too rapidly, by re-heating them to a temperature of about 700° C., and cooling them slowly, as above described.

Examples of the invention follow hereafter:

(*a*) for the MgO-ZnO-Fe_2O_3 system: In a steel ball mill are ground together 412.5 g. Fe_2O_3, 12.5 g. MgO, 75 g. ZnO, 3.25 g. CoO. After 6 hours of grinding, the slip is poured through a 4900 mesh screen (4900 meshes per square cm.) into a porcelain dish and dried. Raw material thus obtained, is pressed, according to ceramic pressing techniques, into rings having dimensions of 59 mm. outside diameter, 35.8 mm. inside diameter, and 12 mm. height, the amount of pressure applied being about 0.5 to 1 t./cm.^{2}. The ferrite pieces thus obtained are sintered in a kiln at 1320° C. for two hours, whereupon the heat is shut off. The rings are cooled to room temperature in the kiln during a period of approximately 24 hours. The ferrite rings thus obtained are provided with 0.4 mm. copper enameled wire with 100 windings as primary winding, and, as secondary winding, further 200 windings with 0.2 mm. copper enameled wire are applied. In the oscillographic photograph of this ferrite, produced in accordance with the invention, which is shown in FIG. 1*a*, one can distinctly recognize the loop constriction of the hysteresis loop.

(*b*) for the MgO-CdO-Fe_2O_3 system: In a steel ball mill are ground together 387.5 g. Fe_2O_3, 25 g. MgO, 87.5 g. CdO, 3.25 g. CoO. After 6 hours of grinding, the slip is poured through a 4900 mesh screen (4900 meshes per square cm.) into a porcelain dish, and dried. Raw material, thus obtained is pressed, according to ceramic pressing techniques, into rings having dimensions

of 59 mm. outside diameter, 35.8 inside diameter, and 12 mm. height, the amount of pressure applied being about 0.5 to 1 t./cm.^{2}. The ferrite pieces thus obtained are sintered in a kiln at 1320° C. for two hours, whereupon the heat is shut off. The rings are cooled to room temperature in the kiln during a period of approximately 24 hours. The ferrite rings thus obtained are provided with 0.4 mm. copper enameled wire with 100 windings as primary winding, and, as secondary winding, further 200 windings with 0.2 mm. copper enameled wire are applied. In the oscillographic photograph of this ferrite, produced in accordance with the invention, which is shown in FIG. 2*a*, one can distinctly recognize the loop constriction of the hysteresis loop.

The following experiment proves that ferrites produced in accordance with the invention are susceptible to thermomagnetic treatment:

The ferrite toroid as prepared in the examples with 100 windings as a primary winding, is placed in a kiln. While heating to 600° C., and slow cooling for 12 hours to room temperature, a longitudinal magnetic field is maintained by means of the ring winding by 1 a. direct current, corresponding to a magnetic field strength of about 15 a.-windings/cm. If the hysteresis loop of the ferrite after this thermomagnetic treatment is recorded in the same manner as described above, the result is analogous to that of metals when they are subjected to heat treatment in the longitudinal magnetic field; a complete change of the form of the hysteresis loop, as may be seen in FIGS. 1*b* and 2*b*, takes place. In analogous manner, heat treatment in the transverse magnetic field may be carried out with corresponding effect (see the above-cited book by Bozorth).

The technical progress obtained with such ferrites in accordance with the invention, may be seen in the following: with thermic longitudinal magnetization, for example, ferrites with distinctly rectangular hysteresis loop may be produced which are of importance to the entire fields of electronics and magnetic amplification, in telephone and high-frequency fields; with thermic cross magnetization, ferrites of high quality and a permeability independent of field strength may be produced, which are particularly suitable for the field of telecommunication.

I claim:

1. A process for preparing cobalt-modified ferrites selected from the class consisting of magnesium-zinc-iron ferrites and magnesium-cadmium-iron ferrite, said ferrites containing 0.1 to 5% by weight of cobalt oxide and over 50 mol percent of iron oxide, the weight proportion of magnesium, zinc and iron oxides in said magnesium-zinc-iron ferrite being within the area A–B–C–D of FIG. 3 of the drawing and the weight proportion of magnesium, cadmium and iron oxides of the magnesium cadmium iron ferrite being within the area A–B–C–D of FIG. 4 of the drawing, comprising preparing a powdered composition consisting essentially of ferric oxide, magnesium oxide, cobalt oxide and an oxide selected from the group consisting of zinc oxide and cadmium oxide in the proportions required to provide at least 50 mol percent of ferric oxide and 0.1 to 5% by weight of cobalt oxide, the remainder being said other specified oxides within the proportion specified, molding said powder composition, firing the molded body at about 1180° C. to about 1400° C., and thereafter slowly cooling the fired body from 700° C. down to room temperature over a period of at least about 12 hours to provide a ferrite body having a constricted hysteresis loop, said ferrites being responsive to thermomagnetic treatment to alter the hysteresis loop characteristics.

2. A fired cobalt-modified ferrite body having a constricted magnetic hysteresis loop, said ferrite body being susceptible to thermomagnetic treatment to alter the hysteresis loop characteristics and being selected from the class consisting of the magnesium-zinc-iron oxide system and the magnesium-cadmium-iron oxide system, said ferrite bodies containing about 0.1 to 5% by weight of cobalt oxide, the iron oxide content of said ferrite body being at least 50 mol percent thereof, the proportion by weight of the magnesium, zinc and iron oxides of the magnesium-zinc-iron ferrite being within the area A–B–C–D of FIG. 3 of the drawing and the proportion by weight of the magnesium cadmium and iron oxides of the magnesium-cadmium-iron ferrite being within the area A–B–C–D of FIG. 4 of the drawing, said ferrite body being prepared by the process of claim 1.

3. A ferrite as defined in claim 2 in which the cobalt oxide content is between 0.35 and 1.0% by weight thereof.

4. A ferrite as defined in claim 3 in which the proportion of magnesium oxide, zinc oxide and iron oxide falls within area A–B–C–D of triaxial diagram of FIG. 3 of the drawing, the corners of said area being as follows:

A=19% MgO, 0% ZnO, 81% Fe_2O_3, by weight,
B=1% MgO, 29% ZnO, 70% Fe_2O_3, by weight,
C=1% MgO, 8% ZnO, 91% Fe_2O_3, by weight,
D=7.5% MgO, 0% ZnO, 92.5% Fe_2O_3, by weight.

5. A ferrite as defined in claim 3, in which the proportion of magnesium oxide, cadmium oxide and iron oxide falls within area A–B–C–D of the triaxial diagram of FIG. 4 of the drawing. The corners of said area being as follows:

A=19% MgO, 0% CdO, 81% Fe_2O_3, by weight,
B=1% MgO, 34% CdO, 65% Fe_2O_3, by weight,
C=1% MgO, 8% CdO, 91% Fe_2O_3, by weight,
D=7.5% MgO, 0% CdO, 92.5% Fe_2O_3, by weight.

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