March 6, 1962 O. ECKERT 3,024,196

FERRITE WITH CONSTRICTED MAGNETIC HYSTERESIS LOOP

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FIG. 1a.

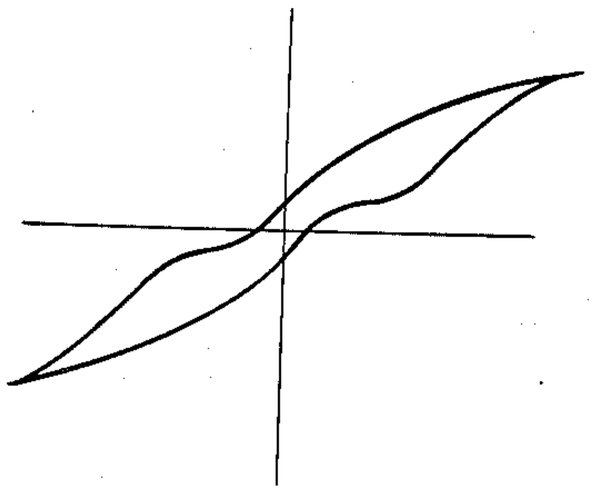


FIG. 2a.

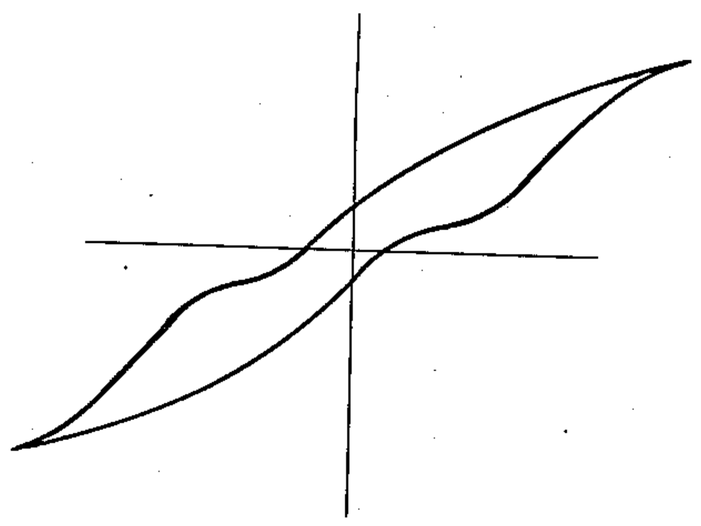
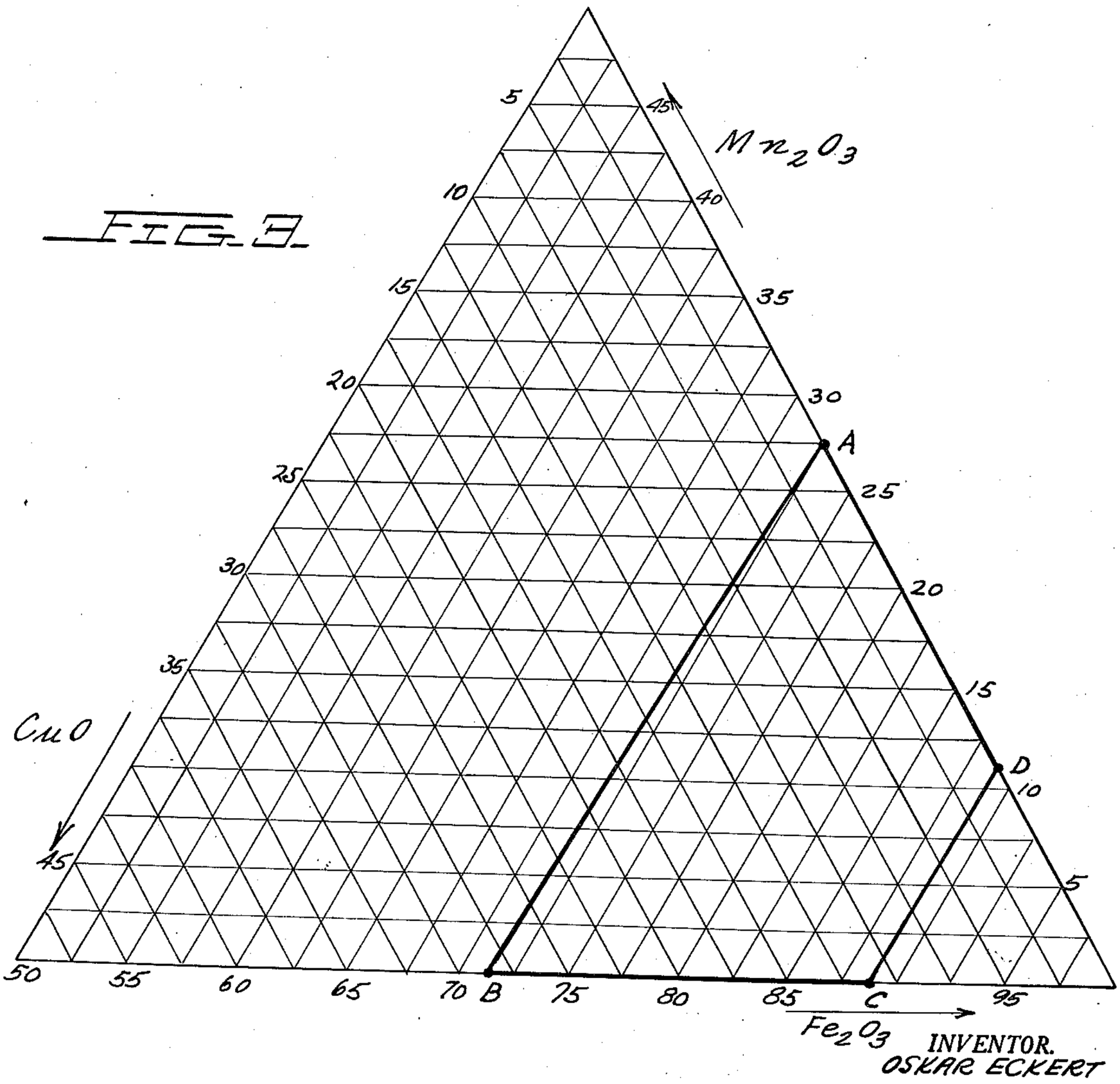


FIG. 3



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FERRITE WITH CONSTRICTED MAGNETIC HYSTERESIS LOOP

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FIG. 1b

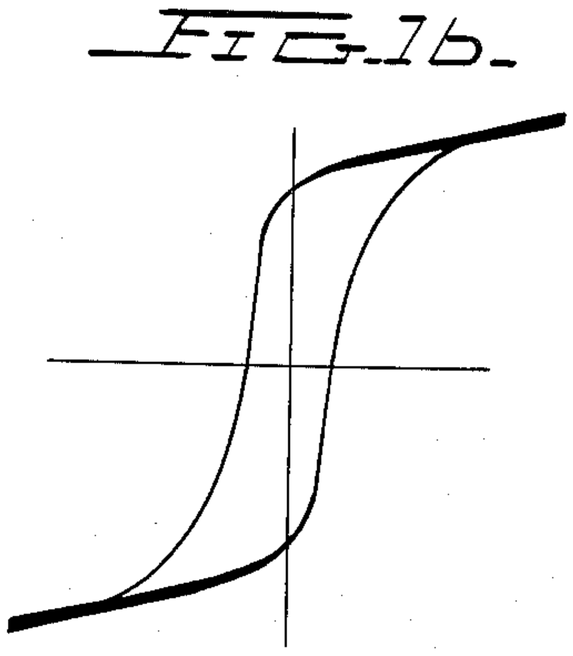


FIG. 2b

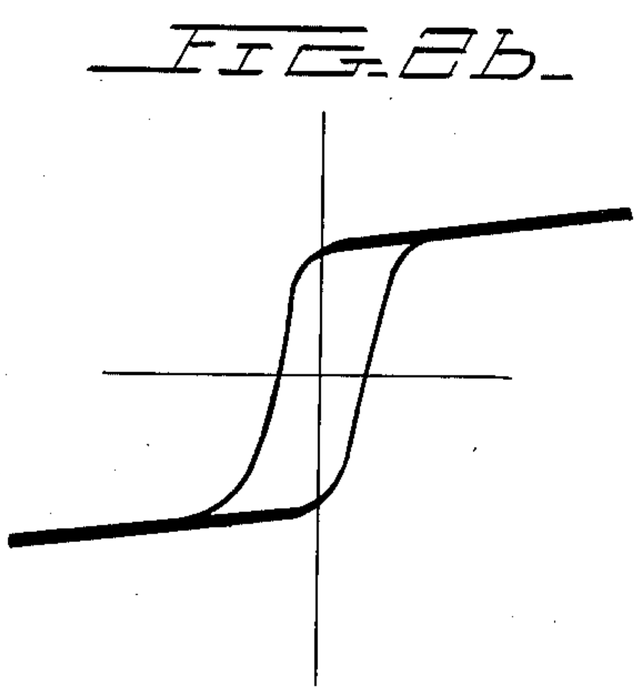
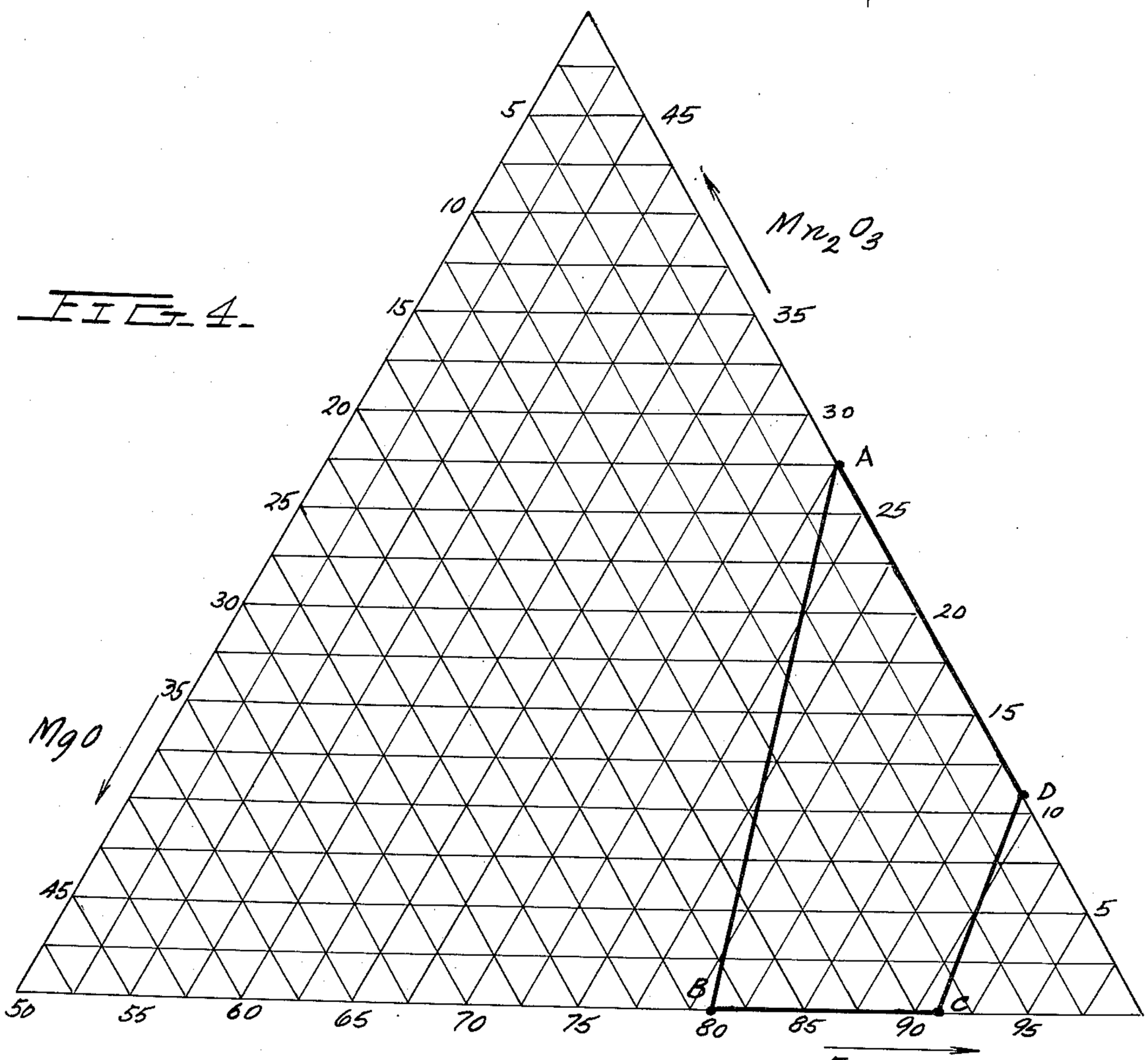


FIG. 4



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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," by D. Van 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 thru a thermic cycle during the simultaneous presence of a longitudinal or transverse magnetic field. In this connection, the concept of longitudinal or transverse field is, 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, or respectively vertical, to the later measuring field. Thru 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.

It has now been found possible to manufacture specific ferrites showing constricted magnetic hysteresis loops which are, consequently, capable of thermomagnetic treatment similarly to metals.

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

In the drawing:

FIG. 1*a* is a reproduction of a constricted hysteresis loop obtained from the Mn—Cu ferrite, of the invention.

FIG. 1*b* is a reproduction of a hysteresis loop obtained by thermal treatment of the ferrite from which FIG. 1*a* was obtained.

FIGS. 2*a* and 2*b* are hysteresis loops corresponding to FIGS. 1*a* and 1*b*, respectively, but obtained from the Mn—Mg ferrite of the invention.

FIG. 3 is a triaxial diagram showing in weight percent the proportion of copper, manganese and ferric oxides in the Cu—Mn ferrite of the invention.

FIG. 4 is a triaxial diagram similar to FIG. 3 for the Mg—Mn ferrite of the invention.

In accordance with the invention, ferrites with this characteristic in the Mn—Cu or Mn—Mg ferrites 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 Mn—Cu or Mn—Mg ferrites 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 Mn—Cu or Mn—Mg 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—Mn_2O_3—CuO or Fe_2O_3—Mn_2O_3—MgO the area defined in the attached diagrams FIGS. 3 and 4, respectively, by the quadrangle

connecting points A, B, C, D. The compositions at the corners in percent by weight are:

(*a*) *For the* Fe_2O_3—Mn_2O_3—CuO *System*

	Fe_2O_3	Mn_2O_3	CuO
A	72.5	27.5	0
B	71.5	0	28.5
C	89	0	11
D	89	11	0

(*b*) *For the* Fe_2O_3—Mn_2O_3—MgO *System*

	Fe_2O_3	Mn_2O_3	MgO
A	72.5	27.5	0
B	81	0	19
C	91	0	9
D	89	11	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 may, after drying, 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 mass or only a part thereof, preferably between 750° C. and 1100° C. for the Mn—Cu ferrite or 750° C. to 1250° C. for the Mn—Mg ferrite. The thus treated parts are sintered, depending on the composition, in a suitable way between 1180° C. and 1350° C. for the Mn—Cu ferrite system or 1250° C. and 1400° C. for the Mn—Mg ferrite. To produce the constricted hysteresis loop in ferrites in accordance with 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 constriction 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:

(*a*) *For the* Mn—CuO—Fe_2O_3 *System*

In a steel ball mill are ground, 400 g. Fe_2O_3, 50 g. Mn_2O_3, 50 g. CuO, and 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. The powder 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 over a period of approximately 24 hours. The ferrite rings thus obtained are provided with 0.4 mm. copper enameled wire with 100 turns as a primary winding, and, as a secondary winding, a further 200 turns with 0.2 mm. copper enameled wire are applied. The oscillographic photograph of this ferrite, produced in accordance with the invention, is shown in FIG. 1*a*, and one can distinctly recognize the constriction of the hysteresis loop.

(b) For the Mn—MgO—Fe_2O_3 *System*

In a steel ball mill are ground, 400 g. Fe_2O_3, 50 g. Mn_2O_3, 50 g. MgO, and 3.25 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. The powder 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 over a period of approximately 24 hours. The ferrite rings thus obtained are provided with 100 turns of 0.4 mm. copper enameled wire as a primary winding, and, as a secondary winding, a further 200 turns with 0.2 mm. copper enameled wire are applied. The oscillographic photograph of this ferrite, produced in accordance with the invention, is shown in FIG. 2*a*, and one can distinctly recognize the 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 from either of the examples with 100 turns 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 ampere direct current, corresponding to a magnetic field strength of about 15 ampere-turns per centimeter. 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*, respectively, 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 field of electronics and for magnetic amplification for 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 manganese-copper-iron ferrites and manganese-magnesium-iron ferrites containing at least 50 mol percent and up to 89% by weight of iron oxide in the case of the manganese-copper ferrite and at least 50 mol percent and up to 91% by weight in the case of manganese-magnesium ferrite, said ferrite containing 0.1 to 5% by weight of cobalt oxide, up to 27.5% by weight of manganese oxide calculated as Mn_2O_3, the remainder of said ferrite composition consisting essentially of a metal oxide selected from the group consisting of copper oxide and magnesium oxide, comprising preparing a powdered composition consisting essentially of ferric oxide, manganese oxide, cobalt oxide and an oxide selected from the group consisting of copper oxide and magnesium 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 1350° 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.

2. A fired cobalt-modified ferrite body having a constricted hysteresis loop, said ferrite body being susceptible to thermomagnetic treatment to change the hysteresis loop characteristics thereof and having a composition selected from the group consisting of the manganese-copper ferrite system and the manganese-magnesium ferrite system, said ferrite containing from at least 50 mol percent up to 89% by weight of ferric oxide where copper is present and from at least 50 mol percent up to 91% by weight of ferric oxide where magnesium is present, from 0.1 to 5% by weight of cobalt oxide, up to 27.5% of manganese oxide calculated as Mn_2O_3 and the remainder of said ferrite consisting essentially of a metal oxide selected from the group consisting of copper oxide and magnesium oxide, said ferrite being made by the process of claim 1.

3. A cobalt-modified ferrite as defined in claim 2 characterized in that the cobalt oxide content is between 0.35 and 1.5% by weight of said composition.

4. A cobalt-modified ferrite as defined in claim 3, in which the ferrite is of the manganese oxide-copper oxide-iron oxide system and in which the proportions of said components come within area A—B—C—D of FIG. 3 of the drawing, the corners of this area defining the following compositions:

A=72.5% Fe_2O_3, 0% CuO, 27.5% Mn_2O_3, by weight,
B=71.5% Fe_2O_3, 28.5% CuO, 0% Mn_2O_3, by weight,
C=89.0% Fe_2O_3, 11.0% CuO, 0% Mn_2O_3, by weight,
D=89.0%, Fe_2O_3, 0% CuO, 11% Mn_2O_3, by weight.

5. A cobalt-modified ferrite as defined in claim 3, in which the ferrite is of the iron oxide-manganese oxide-mangnesium oxide system and in which said components come within area A—B—C—D of FIG. 4 of the drawing, the corners of this area being as follows:

A=72.5% Fe_2O_3, 27.5% Mn_2O_3, 0% MgO, by weight,
B=81% Fe_2O_3, 0% Mn_2O_3, 19% MgO, by weight,
C=91% Fe_2O_3, 0% Mn_2O_3, 9% MgO, by weight,
D=89% Fe_2O_3, 11% Mn_2O_3, 0% MgO, by weight.

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