June 20, 1961 O. ECKERT 2,989,476

FERRITE WITH CONSTRICTED MAGNETIC HYSTERESIS LOOP

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FIG. 1a

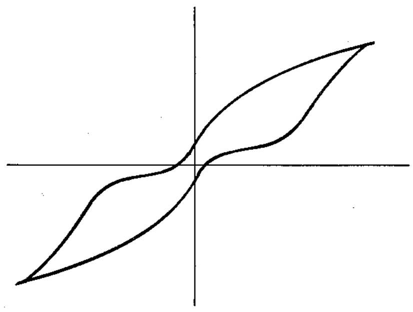

FIG. 1b

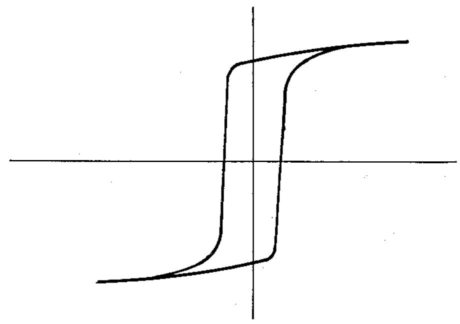

FIG. 3

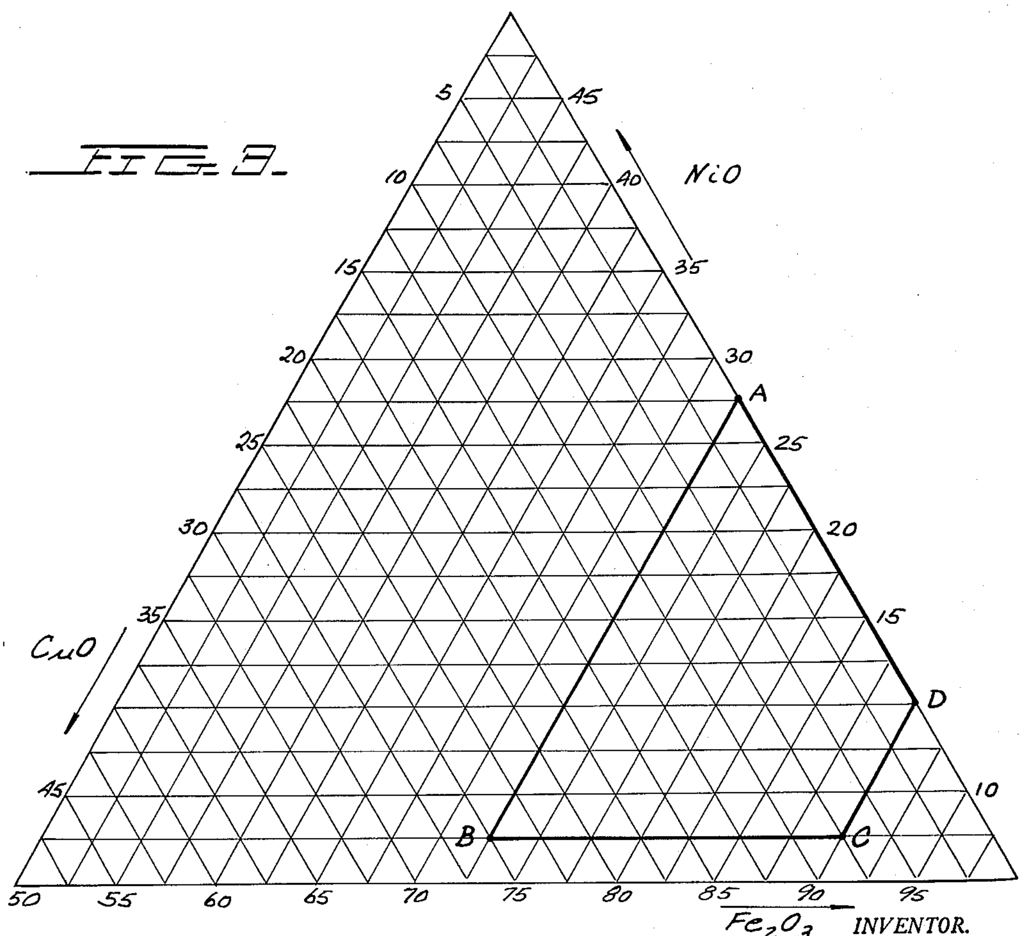

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FIG. 2a

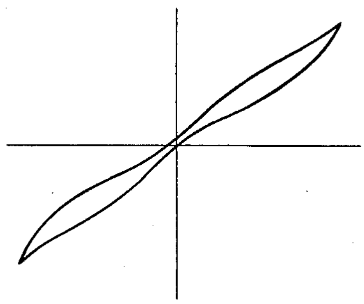


FIG. 2b

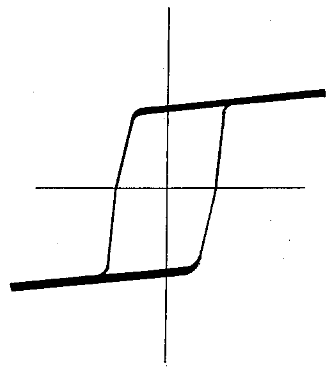
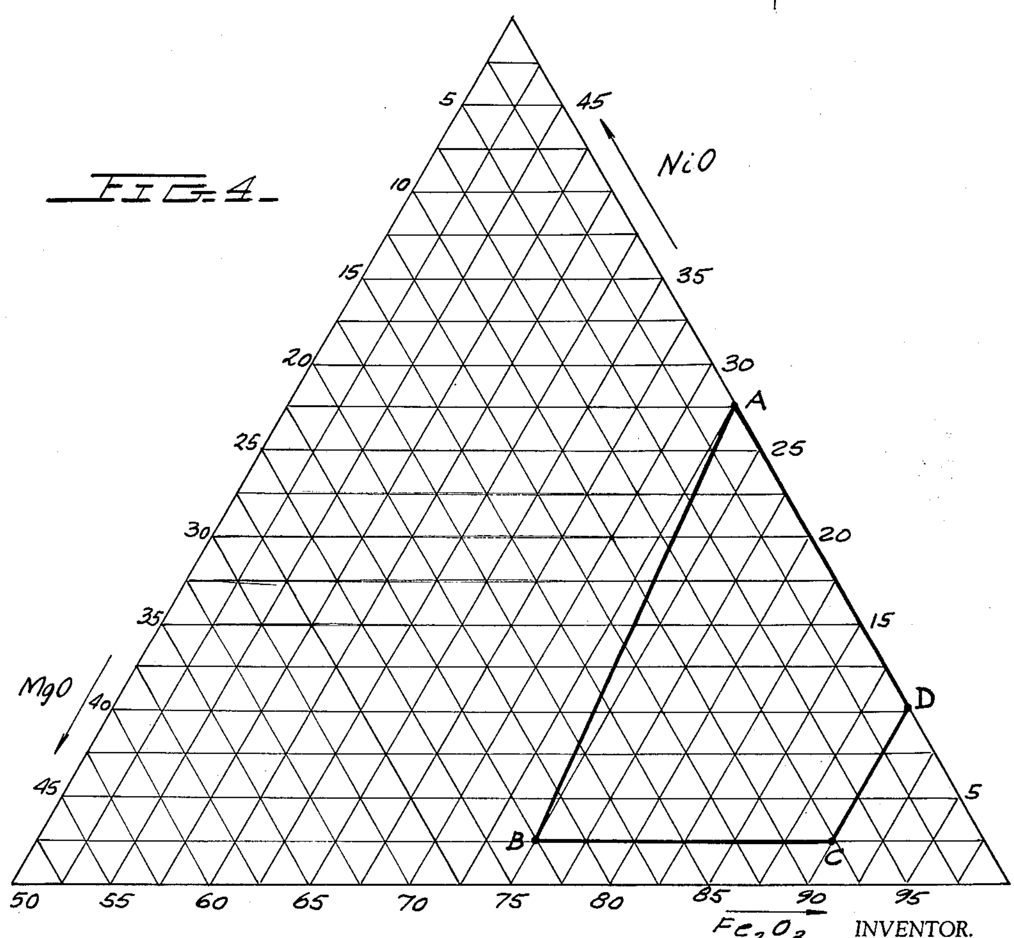


FIG. 4



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2,989,476
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 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. 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 as for metals.

The invention teaches the production of such ferrites of the nickel-copper or nickel-magnesium ferrite-systen. 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 nickel-copper or nickel-magnesium-ferrite-system 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 nickel-copper or nickel-magnesium-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 nickel-copper or nickel-magnesium 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-NiO-CuO or Fe_2O_3-NiO-MgO the area defined in the diagrams of FIGS. 3 and 4, respectively, by the quadrangle points A, B, C, D. The compositions at the corners in percent by weight, are:

(*a*) for the Fe_2O_3-NiO-CuO system:

	Fe_2O_3	NiO	CuO
A	72.5	27.5	0
B	72.5	25	25
C	90.0	2.5	7.5
D	90.0	10.0	0

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

	Fe_2O_3	NiO	MgO
A	72.5	27.5	0
B	75.0	2.5	22.5
C	90.0	2.5	7.5
D	90.0	10.0	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 composition or only a part thereof, preferably between 750° C. and 1100° C. for the Ni-Cu ferrite or 750° C. and 1250° C. for the Ni-Mg ferrite. The resultant parts are sintered, depending on the composition, in a suitable way between 1180° C. and 1350° C. for the Ni-Cu ferrite or 1250° C. and 1400° C. for the Ni-Mg ferrite system. To produce the constricted hysteresis loop in ferrites made 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 constriction does not occur. However, the constriction may be regained even for rings cooled too rapidly, by reheating them to a temperature of about 700° C., and cooling them slowly, as above described.

An example of the invention follows hereafter:

(*a*) for the NiO-CuO-Fe_2O_3 system: In a steel ball mill are ground together 387.5 g. Fe_2O_3, 75 g. NiO, 37.5 g. CuO, 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 resulting ferrite pieces, 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 NiO-MgO-Fe_2O_3 system: In a steel ball mill are ground together 412.5 g. Fe_2O_3, 25.0 g. NiO, 62.5 g. MgO, 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 raw material thus obtained is pressed according to ceramic pressing technique into rings of 59 mm. outside diameter, 35.8 mm. inside diameter, and about 0.5 to 12 mm. high, the amount of pressure applied being about 1 ton per sq. cm. The ferrite raw-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 for 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 of the example 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 for magnetic amplification, for telephone and high-frequency fields; with thermic cross magnetization, ferrities 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 cobalt-modified ferrite with a constricted magnetic hysteresis loop, said ferrite being of the class consisting of nickel-copper-iron and nickel-magnesium-iron systems containing 0.1 to 5% by weight of cobalt oxide, the iron oxide content of said composition being at least 50 mol percent expressed in metal oxides, said ferrite exclusive of the cobalt oxide content containing about 72.5 to 90% by weight of ferric oxide, about 10 to 27.5% by weight of NiO and the remainder consisting essentially of a metal oxide selected from the group consisting of up to 25% by weight of CuO and up to 22.5% by weight of MgO, said ferrite being formed by sintering at about 1180° C. to about 1400° C. and cooling the sintered ferrite from 700° C. down to room temperature over a period of at least twelve hours.

2. The ferrite of claim 1 in which the cobalt oxide content is between 0.35 and 1.5% by weight.

3. The ferrite of claim 2, in which the nickel oxide, copper oxide and ferric oxide is within area ABCD of

FIG. 3 of the drawing, the corners of said area representing the following composition:

A=27.5% NiO, 0% CuO, 72.5% Fe_2O_3, by weight,
B=2.5% NiO, 25% CuO, 72.5% Fe_2O_3, by weight,
C=2.5% NiO, 7.5% CuO, 90% Fe_2O_3, by weight,
D=10% NiO, 0% CuO, 90% Fe_2O_3, by weight.

4. The ferrite of claim 2 in which the composition is within area A'B'C'D' of FIG. 4 of the drawing, the corners of said quadrangular area representing the following compositions:

A=27.5% NiO, 0% MgO, 72.5% Fe_2O_3, by weight,
B=2.5% NiO, 22.5% MgO, 75% Fe_2O_3, by weight,
C=2.5% NiO, 7.5% MgO, 90% Fe_2O_3, by weight,
D=10.0% NiO, 0.0% MgO, 90% Fe_2O_3, by weight.

5. A process for preparing cobalt-modified ferrites selected from the class consisting of nickel-copper-iron ferrites containing at least 50 mol percent of iron oxide plus 0.1 to 5% by weight of cobalt oxide and nickel-magnesium-iron ferrites containing at least 50 mol percent of iron oxide plus 0.1 to 5% by weight of cobalt oxide comprising intimately mixing ferric oxide, nickel 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, molding said powder mixture to shape, firing the molded article 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.

References Cited in the file of this patent

UNITED STATES PATENTS

1,976,230	Kato et al.	Oct. 9, 1934
1,997,183	Kato et al.	Apr. 9, 1935
2,549,089	Hegyi	Apr. 17, 1951
2,568,881	Albers-Schoenberg	Sept. 25, 1951
2,656,319	Berge	Oct. 20, 1953
2,723,239	Harvey	Nov. 8, 1955
2,736,708	Crowley	Feb. 28, 1956
2,778,803	Crowley	Jan. 22, 1957
2,860,105	Gorter et al.	Nov. 11, 1958
2,886,530	Greger	May 12, 1959

FOREIGN PATENTS

1,100,865	France	Apr. 13, 1955
1,125,577	France	July 16, 1956
203,910	Australia	Nov. 1, 1956
510,462	Belgium	Apr. 30, 1952
748,070	Great Britain	Apr. 18, 1936

OTHER REFERENCES

J. Institute of Electrical Engineers, Japan, November 1937, pp. 4, 5, June 1939, pp. 278, 279.

Bozorth: Physical Reviews, Sept. 15, 1955, p. 1792.

Weil: Comptes Rendus v. 234, p. 1352 (1952).

Proceedings of the I.R.E., vol. 44, No. 10 (Ferrites Issue), October 1956, pages 1300, 1301, 1304, 1305 and 1306.

Ferromagnetism, Bozorth, D' Van Nostrand, 1951, pp. 498 and 499 pert.

RCA Review, September 1950, page 345.