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MAGNETIC MATERIALS HAVING RECTANGULAR HYSTERESIS CHARACTERISTICS

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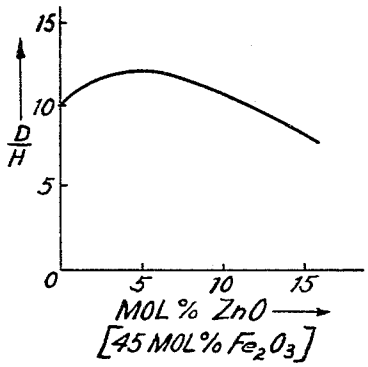


Fig. 1

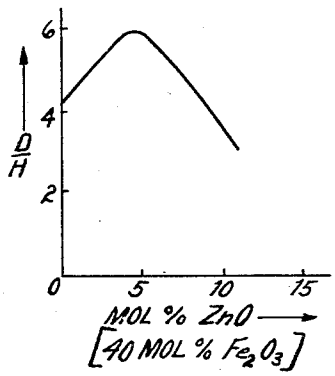


Fig. 3

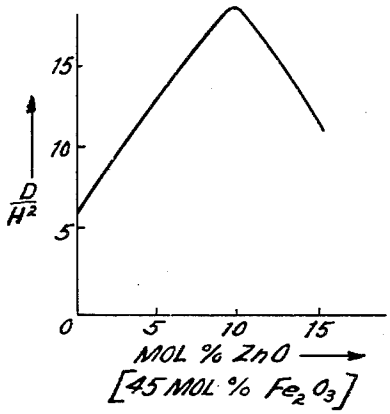


Fig. 2

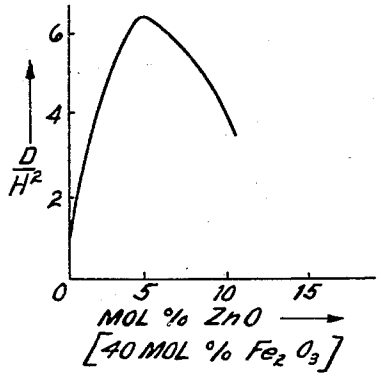


Fig. 4

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MAGNETIC MATERIALS HAVING RECTANGULAR HYSTERESIS CHARACTERISTICS

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This invention relates to improved ferrospinel compositions and methods of making them. More particularly it relates to improved ferrospinel compositions having hysteresis characteristics particularly adapted for use in saturable reactor devices.

The term "ferrospinel" as used herein refers to ferromagnetic oxide compositions, also known as ferrites, which include iron oxide and have essentially a spinel crystal structure. Ferrospinel is more definite than the term "ferrite" which has been used to refer to any compound formed when ferric oxide is combined with a more basic metallic oxide. Ferrite is a broader term than ferrospinel and may be used to refer also to compounds that do not have a spinel crystal structure.

Many different ferrospinel compositions have been prepared and described previously. As a class these compositions exhibit advantageous magnetic properties including high magnetic permeability and low electrical losses. Certain of the previously described materials also have a nearly rectangular hysteresis loop and a low coercive force such that they are especially adaptable for use as saturable reactors. For example, in magnetic memory devices it is desirable to provide a magnetic core that may be saturated by a magnetizing pulse of unit magnitude but substantially unaffected by a magnetizing pulse of ½ unit magnitude. This requirement and the reasons for it are explained in detail in an article by Jan A. Rajchman in the Proceedings of the I.R.E., October 1953, page 1407. Only materials having hysteresis characteristics with a high degree of rectangularity satisfactorily meet this requirement. Previously known materials having substantially rectangular hysteresis loops include ferrospinels of the manganese-magnesium system and manganese-lithium ferrospinels including one or more of magnesium, zinc, cadmium, nickel and copper ferrospinels in solid solution.

One object of the instant invention is to provide novel ferrospinel compositions having improved magnetic characteristics particularly adaptable for use in saturable reactors. A further object is to provide improved methods of making these compositions to optimize their magnetic characteristics.

These and other objects are accomplished according to the instant invention by ferrite compositions comprising 40–47% Fe_2O_3, 40–55% MnO and 5–15% ZnO or CdO on a molar basis. ZnO and CdO are equivalents in the composition of the invention and may be substituted one for the other in any proportion, ZnO being preferred because of cost. The optimum processing temperatures are specified hereinafter for several specific compositions within the scope of the invention. In general, optimum results are provided when the compositions are heated at about 1075° to 1275° C. for about one hour. After the compositions are fired they are cooled relatively rapidly by withdrawing them from the furnace and exposing them to the atmosphere at ordinary room temperatures.

The invention will be described in greater detail in

connection with the accompanying drawing of which:

Figure 1 is a line graph illustrating the variation in a quality factor as a function of the zinc content of several compositions of the invention;

Figure 2 is a line graph of a different quality factor from that shown in Figure 1 but with respect to the same compositions and as a function of the same variant; and,

Figures 3 and 4 are line graphs of the same quality factors described in Figures 1 and 2, respectively, but showing the variations of the quality factors in different compositions from those shown in Figures 1 and 2.

The compositions of the instant invention may be initially prepared in a manner similar to other ferrospinel compositions. Raw metallic oxides or their equivalents are mixed together and pulverized as by wet milling in a ball mill for one hour or more. Generally, it is not necessary to use the metallic oxides themselves as raw ingredients. Equivalent quantities of any compounds that will decompose at elevated temperatures to yield the desired oxides may be substituted therefor. For example, where extreme purity is desired it is preferred to use manganese carbonate instead of any of the commercially available forms of manganese oxide.

The milled oxide mixture is dried and calcined by heating it at about 900° C. for about one hour. After calcining, the mixture is again milled to reduce its particle size and to insure intimate mixing of the oxides.

An organic binder such as paraffin or a resin and a lubricant such as stearic acid are usually added to the mixture to facilitate molding. The particular binder and lubricant used are not critical. About 4% by weight of a 50% water suspension of paraffin may be used as a binder and about 1% by weight stearic acid may be added as a mold lubricant, the weight percents being based on the total weight of the final mixture. The mixture is molded into core bodies by any convenient method such as by pressing in a die, after which the molded bodies are heated at about 400° to 500° C. to burn off the binder and the lubricant. The bodies are then fired for about one hour at a temperature between 1075° and 1275° C. The firing temperatures are relatively critical to provide optimum electrical properties in the compositions. A change of 25° C. almost invariably seriously affects the electrical properties of the materials, and in some cases, a change of as little as 5° C. may reduce the electrical properties to below commercially acceptable limits. The time for which the bodies are held at their firing temperatures, on the other hand, has been found not to be critical. This is shown, for example, by the composition code number 5 listed in the table, which was fired for 18 hours and still exhibits excellent electrical properties.

A representative group of different compositions within the scope of the instant invention is listed in the table.

TABLE

Code No.	Composition—Mol. Percent			Firing Temp., °C.	D	H	D/H	D/H²
	Fe_2O_3	ZnO or CdO	MnO					
1	40	5	55	1,075	5	0.9	5.6	6.2
2	40	10	50	1,175	2.5	0.8	3.1	3.9
3	40		60	1,125	14	3.3	4.2	1.3
4	45	5	50	1,175	14	1.1	13.4	12.7
5	45	10	45	[1] 1,175	6	0.6	10	16.6
6	45	15	40	1,275	4.5	0.6	7.5	12.5
7	45		55	[2] 1,125	18	1.75	10.3	5.8
8	47	5	48	1,200	4	0.7	5.7	8.2

[1] Fired for 18 hours. Indicates that firing time over 1 hour is not critical.
[2] Fired and cooled in nitrogen atmosphere.

All of these compositions may be prepared according to the general method heretofore described using the specified ingredients and firing temperatures indicated in the table. The firing time is one hour for all the compositions except No. 5. For example, the composition identified by the code No. 4 may be made by mixing iron oxide, zinc oxide and manganese oxide in the mole proportions of:

.45 Fe_2O_3
.05 ZnO
.50 MnO

About 1 lb. of the mixed oxides may be placed in a steel ball mill with about a pint of water or alcohol and milled for about one hour. The milled mixture is calcined by heating it in air or an ordinary kiln atmosphere at about 1000° C. for about one hour. The calcined mixture, now at least partly reacted and comprising a substantial proportion of a ferrospinel composition together with some unreacted oxides is again wet ground in a ball mill for at least one hour and preferably for about six hours. About 4% by weight of a 50% water emulsion of paraffin and about 1% by weight Trigamine oleate are added to the mixture after it is ground and dried. The paraffin serves as a binder and the oleate as a mold lubricant in the subsequent molding step. The resulting mixture is a relatively thin paste which is dried so that it may be directly molded or cut into pellets for greater convenience in molding. The mixture in bulk or pellet form is molded by pressing in a die to form a shaped core body such as a toroid, or annulus. The core bodies are heated at about 400° to 500° C. to burn off the binder and the lubricant. They are then placed in a high temperature kiln where they are heated to about 1175° C. and maintained at that temperature for about one hour. After one hour the bodies are withdrawn from the kiln and exposed to the atmosphere at room temperature so that they may be rapidly cooled.

The cooling step is preferably accomplished as rapidly as can possibly be done without damaging the core bodies. Generally, the bodies must be left on their setter plates for cooling; otherwise they may cool so rapidly that they develop cracks due to thermal strains. If the bodies are cooled slowly their electrical properties are usually adversely affected, especially if they are cooled in an air, or other oxidizing atmosphere. This effect appears to be due to the unstable, ambivalent nature of manganese. At the firing temperature the manganese, it is believed, assumes lattice sites corresponding to an optimum, but unknown, state of oxidation. If the bodies are cooled slowly the manganese has an opportunity to reorient itself in the crystal structure in less advantageous positions, or to change its condition in some other manner due to its tendency to assume different oxidation states at different temperatures. When the bodies are quenched, on the other hand, the manganese is "frozen" in the position and oxidation state it assumed at the firing temperature.

For purposes of comparing the magnetic properties of the materials of the invention test toroids of the materials are prepared as heretofore described. They are all made of a uniform size, having an outside diameter of about 0.5 cm., an inside diameter of 0.3 cm. and a height of about 0.1 cm. They are wound with a primary, input winding of five turns and a secondary, output winding of one turn, each of A.W.G. No. 33 copper wire. The hysteresis characteristics of the materials are determined by a pulse technique such as that described by Jan A. Rajchman in an article in the RCA Review, June 152, pages 196–198. The values given in the table for D and H are the discrimination and the optimum input, in ampere-turns, taken from such tests. Although the parameter, D, or discrimination has no well-accepted, precise definition it may be approximately described as the maximum possible ratio between the remanence flux changes of two hysteresis loops, one of the loops being generated by an alternating current of unit magnitude, and the other one being generated by an alternating current of one-half unit magnitude. In most known material this ratio varies according to the absolute value of the unit magnitude, some materials requiring a relatively large driving current to maximize the ratio, others requiring a relatively small driving current. H is the driving current, expressed as ampere-turns, that results in the maximum ratio, or optimum discrimination.

Due to variations in individual test techniques the values of D as determined by different experimenters cannot be expected to match perfectly. They should, however, correspond in that, for any two given materials, all methods of determining D will agree as to which one is better than the other. The values of D stated herein are, therefore, relative only, and are not intended as absolute values.

The composition of a suitable figure of merit taking both discrimination and driving current into account is somewhat arbitrary and may depend upon the specific circuit application in which the material is to be used. Two figures of merit are shown herein, one being a simple ratio of D/H, the other being a ratio of D/H^2. In those cases where discrimination is of maximum importance and relatively large driving currents are readily available the first figure of merit may be preferred. On the other hand where the driving current restriction are relatively severe, the second figure of merit may be preferred.

The variations of these two figures of merit are shown in the drawing as functions of the various compositions shown in the table. Figure 1 describes the first figure of merit, D/H, as a function of the zinc oxide proportion in ferrospinel compositions including manganese oxide and 45 mol. percent iron oxide. It will be noted that the quality figure is at a maximum when the zinc oxide comprises about 5% of the total composition. Figure 2 illustrates the variation of the second figure of merit, D/H^2, with respect to the same compositions described in Figure 1. This curve shows a relatively sharp maximum at about 10% zinc oxide. Figure 3 corresponds in general to Figure 1 except that the compositions of Figure 3 comprise only 40 mol. percent Fe_2O_3 instead of 45 mol. percent. Again it will be noted that in these compositions, also, the D/H figure of merit reaches a maximum at about 5% zinc oxide. Figure 4 describes the variation of the second figure of merit, D/H^2, with respect to the same compositions as described in Figure 3. It, too shows a maximum at about 5% zinc oxide concentration.

Except for the firing temperature the processing of the compositions of the invention is not critical but may be accomplished according to conventional techniques. The oxides, for example, instead of being ground initially to pulverulent form may be precipitated from an aqueous solution in such form that they require no further grinding. Other steps also may be varied according to known principles such as, for example, the substitution of different binders from those heretofore described and the use of different pressing or molding techniques.

The compositions of the invention are novel and are believed to offer advantageous properties not heretofore available in other materials previously available for the same uses. In particular, these compositions require very low driving currents, and have relatively high remanence characteristics which provide relatively high output voltage capabilities.

There have thus been described improved ferrospinel compositions and methods of making them, which compositions are particularly adapted for use in saturable reactors.

What is claimed is:

1. Magnetic composition having a substantially rectangular hysteresis characteristic prepared by firing between 1075° and 1275° C. for at least about one hour and

then rapidly cooling a formed body consisting essentially of:

	Mol. percent
Fe_2O_3	40–47
At least one material selected from the group consisting of ZnO and CdO	5
MnO	Balance

2. Magnetic composition having a substantially rectangular hysteresis characteristic prepared by firing between 1075° and 1275° C. for at least about one hour and then rapidly cooling a formed body consisting essentially of:

	Mol. percent
Fe_2O_3	45–47
At least one material selected from the group consisting of ZnO and CdO	4–15
MnO	40–50

3. Magnetic composition having a substantially rectangular hysteresis characteristic prepared by firing between 1075° and 1275° C. for at least about one hour and then rapidly cooling a formed body consisting essentially of on a molar basis about 40% Fe_2O_3, 55% MnO and 5% of at least one material selected from the group consisting of Zno and CdO.

4. Magnetic composition having a substantially rectangular hysteresis characteristic prepared by firing between 1075° and 1275° C. for at least about one hour and then rapidly cooling a formed body consisting essentially of on a molar basis about 45% Fe_2O_3, 50% MnO and 5% of at least one material selected from the group consisting of ZnO and CdO.

5. Magnetic composition having a substantially rectangular hysteresis characteristic prepared by firing between 1075° and 1275° C. for at least about one hour and then rapidly cooling a formed body consisting essentially of on a molar basis about 45% Fe_2O_3, 45% MnO and 10% of at least one material selected from the group consisting of ZnO and CdO.

6. Magnetic composition having a substantially rectangular hysteresis characteristic prepared by firing between 1075° and 1275° C. for at least about one hour and then rapidly cooling a formed body consisting essentially of on a molar basis about 45% Fe_2O_3, 40% MnO and 15% of at least one material selected from the group consisting of ZnO and CdO.

7. Magnetic composition having a substantially rectangular hysteresis characteristic prepared by firing between 1075° and 1275° C. for at least about one hour and then rapidly cooling a formed body consisting essentially of on a molar basis about 47% Fe_2O_3, 48% MnO and 5% of at least one material selected from the group consisting of ZnO and CdO.

8. Method of making a magnetic material having a substantially rectangular hysteresis characteristic comprising mixing together pulverulent metallic oxides in the molar proportions of about 40% Fe_2O_3, 55% MnO and 5% of an oxide selected from the group consisting of ZnO and CdO, molding said mixed oxides to form a shaped body and firing said shaped body at about 1075° C. for at least one hour thereby to react said oxides and to sinter said body, and rapidly cooling said body from its firing temperature.

9. Method of making a magnetic material having a substantially rectangular hysteresis characteristic comprising mixing together pulverulent metallic oxides in the molar proportions of about 45% Fe_2O_3, 50% MnO and 5% of an oxide selected from the group consisting of ZnO and CdO, molding said mixed oxides to form a shaped body and firing said shaped body at about 1175° C. for at least one hour thereby to react said oxides and to sinter said body, and rapidly cooling said body from its firing temperature.

10. Method of making a magnetic material having a substantially rectangular hysteresis characteristic comprising mixing together pulverulent metallic oxides in the molar proportions of about 45% Fe_2O_3, 45% MnO and 10% of an oxide selected from the group consisting of ZnO and CdO, molding said mixed oxides to form a shaped body and firing said shaped body at about 1175° C. for at least one hour thereby to react said oxides and to sinter said body, and rapidly cooling said body from its firing temperature.

11. Method of making a magnetic material having a substantially rectangular hysteresis characteristic comprising mixing together pulverulent metallic oxides in the molar proportions of about 45% Fe_2O_3, 40% MnO and 15% of an oxide selected from the group consisting of ZnO and CdO, molding said mixed oxides to form a shaped body and firing said shaped body at about 1275° C. for at least one hour thereby to react said oxides and to sinter said body, and rapidly cooling said body from its firing temperature.

12. Method of making a magnetic material having a substantially rectangular hysteresis characteristic comprising mixing together pulverulent metallic oxides in the molar proportions of about 47% Fe_2O_3, 48% MnO and 5% of an oxide selected from the group consisting of ZnO and CdO, molding said mixed oxides to form a shaped body and firing said shaped body at about 1200° C. for at least one hour thereby to react said oxides and to sinter said body, and rapidly cooling said body from its firing temperature.

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