April 24, 1962 H. A. DI MARCO 3,031,407

METHOD OF PRODUCING FERRITE BODIES

Filed March 24, 1959 2 Sheets-Sheet 1

FIG. 1

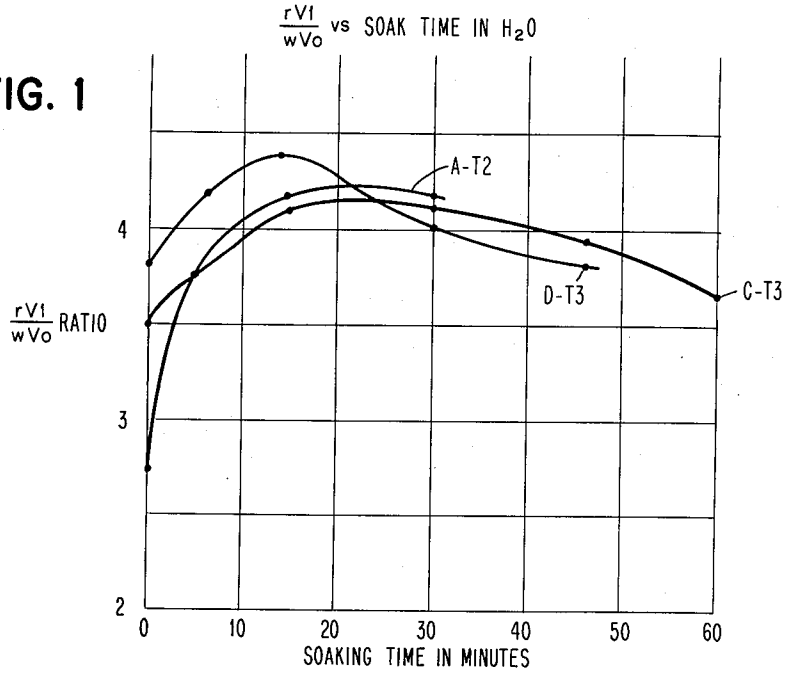


FIG. 3

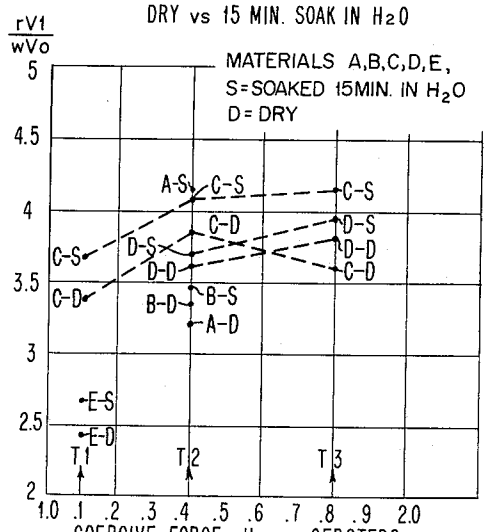
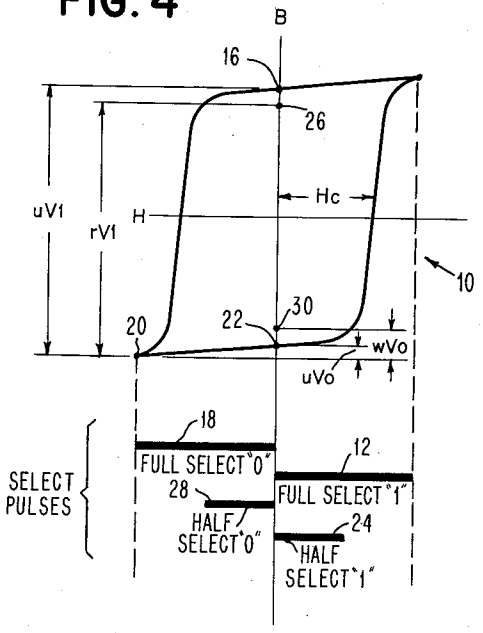


FIG. 4



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April 24, 1962 H. A. DI MARCO 3,031,407

METHOD OF PRODUCING FERRITE BODIES

Filed March 24, 1959 2 Sheets-Sheet 2

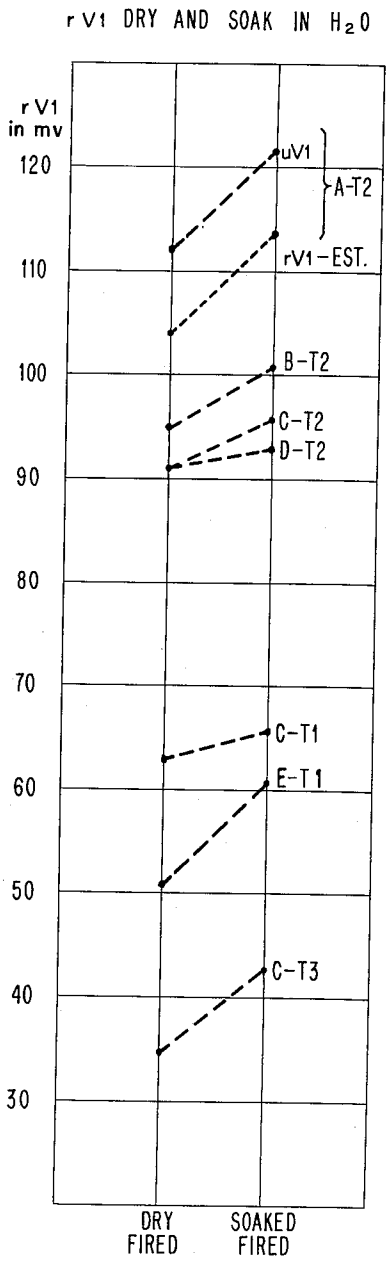
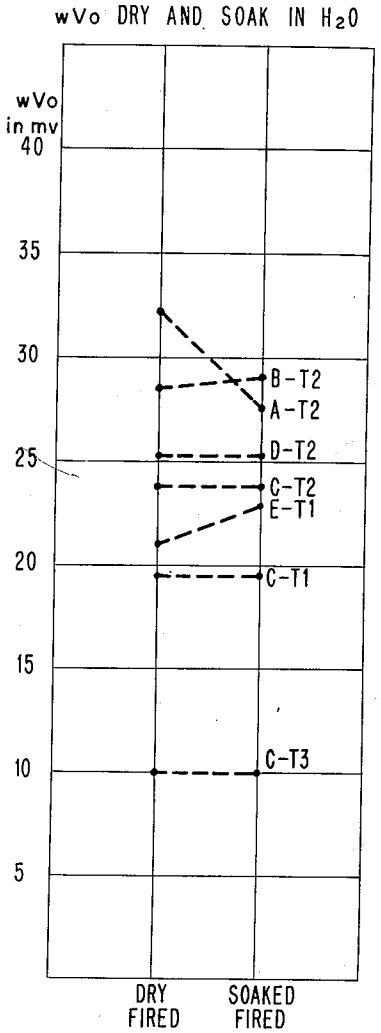


FIG. 2a

FIG. 2b



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METHOD OF PRODUCING FERRITE BODIES

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13 Claims. (Cl. 252—62.5)

This invention relates to ferrite magnetic materials of the spinel type generally referred to as ferrospinels, and relates particularly to an improved method for processing bodies of such materials so as to provide bodies having improved squareness of the hysteresis characteristic.

Ferrospinel bodies are employed as magnetic memory elements and as pulse transfer elements in computers and other data processing apparatus. When the ferrospinels are employed as memory devices, the squareness of the hysteresis characteristic is of particular importance. The most usual application requiring a maximum of hysteresis squareness is the application involving the use of ferrospinel bodies for coincident current memory devices in which the bodies have a high degree of squareness making it possible to switch the magnetic state of the bodies upon the occurrence of two simultaneously existing current pulses, one of which alone is of insufficient intensity to produce magnetic switching. This type of memory device is well-known in the art.

Ferrospinel bodies are produced by sintering bodies pressed from mixed powders of ferric oxide and one or more bivalent metal oxides. During the sintering operation, the constituents of the molded bodies arrange themselves to form a spinel type crystal structure. Process and compositions for producing these ferrospinel structures are well-known.

The primary object of the present invention is to improve the squareness characteristic obtained from these spinel type crystal structures and this improvement is brought about by soaking the pressed body in water before the body is sintered.

As previously noted, a square loop memory body desirably exhibits a maximum possible amount of squareness in order that its magnetic state will be substantially undisturbed by a pulse having one half the intensity of a pulse capable of changing the magnetic state of the body. In all such bodies, however, there is some degree of disturbance resulting from half select pulses being applied thereto. The result of this disturbance is to reduce, to some degree, the density of magnetization retained by the body.

The body is capable of retaining one of two opposite states of magnetization, one of these may be considered as being a "1" state and the other may be considered as being a "0" state. When a body is driven from one of these states to the other by means of the application of a magnetic driving force, an output is produced which may be sensed on a suitable sense line and the degree of the output may be measured in millivolts. Thus, if a body is in the "1" state and it has applied thereto a driving pulse to drive it to a "0" state, there will be produced what may be termed as a full select or undisturbed output voltage $_{u}V_1$. On the other hand, if the body was in the "0" state and a full select "0" driving pulse is applied, there will be produced only a very small resulting select output voltage $_{u}V_0$.

If a body is in the "1" state and a half select "0" drive pulse is applied, the net result will be to reduce the degree of magnetization remaining in the body. The extent of this reduction will be determined by the squareness of the hysteresis loop of the body. In view of the fact that a body used as a coincident current device may receive a plurality of half select pulses before receiving a full select pulse, the reduction by each pulse must be

kept as small as possible to minimize the diminution of the full select output signal.

Similarly, if the body is in the "0" state and a half select "1" drive pulse is applied, the degree of magnetization in the "0" direction will also be reduced. This reduction in magnetization gives rise to an output upon a "0" selection which appears as a noise signal and must therefore be minimized.

As will be hereinafter more fully described, the hysteresis squareness of a body may be defined as the ratio of the output of switching from a disturbed "1" state to the "0" state, expressed as $_{r}V_1$, divided by the output of switching from a disturbed "0" state to the "0" state, expressed as $_{w}V_0$.

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of specific embodiments of the invention as illustrated in the accompanying drawings.

In the drawings:

FIGURE 1 is a chart showing the effect of soaking time in minutes on the $_{r}V_1/_{w}V_0$ ratio of ferrospinel bodies;

FIGURE 2*a* is a chart showing respective $_{r}V_1$ values of ferrospinel bodies of various compositions produced from unsoaked moldings and from soaked moldings;

FIGURE 2*b* is a chart showing respective $_{w}V_0$ values of ferrospinel bodies of various compositions produced from unsoaked moldings and from soaked moldings;

FIGURE 3 is a chart showing the comparative $_{r}V_1/_{w}V_0$ ratios of soaked and unsoaked bodies made of various materials and processed to provide various coercivities;

FIGURE 4 shows a hysteresis loop and indicates diagrammatically full and half select pulses for switching a body represented by the loop and from one magnetic state to another.

As has been previously noted, ferrospinel bodies employed as magnetic memory elements are desirably possessed of a square hysteresis characteristic. In FIGURE 4, there is indicated generally at **10**, a hysteresis loop of such a body. The loop is drawn on conventional B and H coordinates. If there is applied to the body a full select "1" driving force on the H axis as indicated by the pulse **12**, the body will be driven to a +B state or a "1" state as indicated by the point **14** on the loop, and, when the driving force is relieved, the residual magnetism in the core will be at a value indicated by the point **16** on the B axis. Similarly, if a full select "0" drive pulse **18** is applied to the body, the magnetic state of the body will be switched to a (—) B state or the "0" state as indicated by the point **20** on the loop, and, when the driving force is relieved, the body will retain a residual magnetism indicated by the point **22** on the B axis.

If, while the body represented by the loop has a residual magnetism of value indicated by the point **16**, a half select "0" pulse as indicated at **28** is applied thereto and then relieved, the degree of magnetism thereafter remaining in the body may, for example, be indicated by the point **26**. Similarly, if when the body is at a magnetic state indicated by the point **22**, a half select "1" pulse **24** is applied thereto and relieved, the magnetic state of the body remaining thereafter may, for example, be indicated by the point **30**. It should be noted that the actual points **26** and **30** shown on the diagram are exaggerated displacements which are selected for the purpose of clarity and are not intended to be indicative dimensionally of any exact condition prevailing for any given body.

When the body is at a magnetic state as indicated by the point **16**, the application of a full select "0" pulse **18** will produce an output voltage indicated by the dimension $_{u}V_1$. If the same full select "0" pulse is applied

when the body had a residual state as indicated by the point 26, a lesser output voltage will be generated. This voltage is indicated at ${}_{r}V_1$. Similarly, if the magnetic body had a residual state as indicated by the point 22 and a full select "0" pulse 18 were applied, an output voltage ${}_{u}V_0$ would be generated, and if the magnetic state had been at the point indicated at 30, upon an application of a full select "0" pulse, an output would have occurred as indicated at ${}_{w}V_0$. It will be evident that the degree of squareness is indicated by the displacement between points 22 and 30, and by the displacement between points 26 and 16.

The ratio ${}_{r}V_1/{}_{w}V_0$ provides a highly satisfactory measure of squareness in that ${}_{w}V_0$ is a relatively absolute value of disturbance resulting from lack of perfect squareness and ${}_{r}V_1$ accommodates for the fact that various materials will have hysteresis loops of various BH ratios. Thus, for a high value of B, a greater displacement between points 22 and 30 may be tolerated than for a low value of B. Accordingly, hereinafter, squareness ratio will be merely referred to as the expression ${}_{r}V_1/{}_{w}V_0$ and the following discussion will consider only values of ${}_{r}V_1$ and ${}_{w}V_0$ in the considerations of this squareness ratio.

The usual techniques employed in the production of ferrospinel bodies involve the mixing of commercially pure fine particles of oxides of desired materials in desired proportions. Such mixing is accomplished, for example, by wet ball milling to form a slurry. The slurry is thereafter dried and the resulting dry cake is ground to a fine powder. This powder is then placed in a suitable container and calcined in air at temperatures of approximately from 600° C. to 1000° C. for time intervals ranging from 30 minutes to 180 minutes. The actual temperatures and times employed vary with the compositions involved.

After calcining, the material is again milled and there is added to the material suitable binder and lubricant materials to facilitate the subsequent molding operation. The binder may be polyvinyl alcohol added in the amount of approximately 3% by weight and the lubricant may be a dibutyl phthalate added in the amount of approximately ¼% by weight.

The resulting mixture is then molded into the form of a desired body which may be of toroidal or of other desired shape. The body in this condition is termed a "green" body.

After the molding operation the "green" body is heated to approximately 600° C. and the binder and lubricant which are organic compounds, are driven therefrom.

After the binder and lubricant are driven off, the "green" molding is soaked in water. The molding at this stage has sufficient physical stability to withstand water soaking without adverse effect on the physical dimensions of the body, and, when water soluble materials such as alcohols are used in the molding, the bodies tend to disintegrate in water if the alcohol has not been driven off prior to soaking. As will be evident from FIGURE 1, which will be described in detail hereinafter, a wide range of soaking times may be employed and while the optimum time varies somewhat depending on the compositions of the powders in the pressed body, a soaking time of from 10 to 30 minutes will generally produce optimum results. Beneficial results can be obtained by a soaking time of from 3 to 50 minutes, the degree of benefit derived therefrom again depending to some degree on the particular compositions of the bodies being treated.

After the soaking step is completed, the wet ferrite body is placed in a furnace and sintered at temperatures ranging from approximately 1100° C. to 1500° C. for time intervals ranging from 15 to 30 minutes depending upon its composition and the characteristics desired. After the sintering step, the sintered body is removed from the furnace and either left to cool in air or, in some instances, furnace cooled to an intermediate temperature of approximately 960° C. and then cooled in air to room temperature.

The foregoing process steps of mixing, calcining, adding binders and lubricants, molding and sintering are well-known in the art. The novel process operation disclosed herein is the soaking operation which, as will be shown in FIGURES 1, 2*a*, 2*b*, and 3 hereinafter described, provides highly beneficial results in the form of improved squareness of the hysteresis characteristic of the ferrospinel body produced by the process.

In FIGURES 1–3, there are shown five compositions processed with and without the benefit of this invention. These compositions are designated as A–E in the following chart showing mol percentages of the various constituents thereof.

Composition	Fe_2O_3	MnO	MgO	CuO	NiO	CrO
"A"	40	22.5	37.5	------	------	------
"B"	44.4	51.11	------	4.44	------	------
"C"	40	55	------	5.0	------	------
"D"	38	57	------	------	2.0	3.0
"E"	38.5	61.5	------	------	------	------

These five compositions are variously processed in order to provide ferrite bodies having three different coercivities. These three coercivities are indicated at T1, T2, and T3, below as 1.1; 1.4; and 1.8, respectively. These coercivities are obtained by firing the compositions at temperatures as indicated in the following chart.

T1, H_c=1.1: C and E fired at 1310° C.
T2, H_c=1.4:
A fired at 1445° C.
B fired at 1275° C.
C fired at 1275° C.
D fired at 1280° C.
T3, H_c=1.8:
C fired at 1240° C.
D fired at 1225° C.

In FIGURE 1, there is plotted the effect of soaking time, i.e., time of soaking the "green" body in water prior to sintering, versus the resulting body squareness as defined by the ${}_{r}V_1/{}_{w}V_0$ ratio. Curves are plotted for material A in type 2 (A–T2), material C in type 3 (C–T3) and material D in type 3 (D–T3).

The data employed in FIGURE 1 was derived from tests made independently of the test from which the data of FIGURES 2*a*, 2*b*, and 3 was derived. It will be noted that while this gives rise to certain discrepancies in actual data values shown, the benefits obtained by the invention are clearly evident in all of the tests. Each of the data points shown in the drawings represents an average taken from a plurality of bodies of a firing. The ${}_{r}V_1$ and ${}_{w}V_0$ values shown in the drawings were obtained from bodies having been subjected to a plurality of half select pulses as follows:

	Half select pulses
T1 bodies	128
T2 bodies	8
T3 bodies	32

It will be observed that the curves of FIGURE 1 indicate a peaking for all of the compositions treated in the general range of 10 to 30 minutes of soaking time, however, the curves also show that even small soaking times, i.e., soaking time of the order of 3 minutes, are highly beneficial, and, extended soaking, i.e., soaking up to one hour still provides some beneficial results.

As is evidenced from FIGURE 1, a soaking time of approximately 15 minutes represents the soaking time at which approximately maximum beneficial results are obtained in each of the compositions tested. Accordingly, this time interval has been taken as the common time interval for all of the tests described in connection with FIGURES 2*a*, 2*b*, and 3.

In FIGURE 2*a*, there is indicated by lines C–T3, C–T1,

etc., a relation between the ${}_rV_1$ value in millivolts for dry fired cores and for cores soaked before firing. The data points for the A–T2 line are established from test for the ${}_uV_1$ value. The ${}_rV_1$ value points for A–T2 shown in FIGURE 2*a* are estimated points. It is believed, however, that this estimate is reasonably accurate for the reason that experience has shown that in this range the ${}_rV_1$ value is approximately 8 millivolts below the ${}_uV_1$ value. Furthermore, in the ultimate ratio number, the numerator of the ${}_rV_1/{}_wV_0$ fraction being relatively large compared to the denominator and can be varied slightly without causing an appreciable difference in the ultimate ratio figure.

In FIGURE 2*b*, there are shown by lines C–T3, D–T1, etc., data points representing the ${}_wV_0$ millivolt value of the respective bodies when fired dry and when soaked before firing.

FIGURE 3 employs the data points shown in FIGURES 2*a* and 2*b*, and indicates the changes in ${}_rV_1/{}_wV_0$ ratio for dry fired and soaked bodies of various compositions when processed to provide body types T1, T2, and T3 having coercivities as indicated in the chart. In this chart, the arrow T1 indicates core type T1, which is of 1.1 coercivity and above this arrow are data points indicated as E–S and E–D, which are E composition soaked and E composition dry, respectively. Also above the T1 arrow are data points C–S and C–D, which are composition C soaked and composition C dry, respectively. The other data points on the chart are similarly noted. From this chart, it will be evident that in every case, the soaked core has a substantially higher ${}_rV_1/{}_wV_0$ than the non-soaked body, thus indicating a substantial improvement of squareness as defined by the ${}_rV_1/{}_wV_0$ ratio.

By use of water soaking, yields from many batches of A–T2 bodies, have improved in acceptability by 10 to 20% indicating that improved uniformity as well as improvide maximum squareness results by use of the water soaking.

The ferrospinel material exhibiting square hysteresis loop characteristics is a manganese ferrite system (Magnetic and Electrical Properties of the Binary Systems $MO.Fe_2O_3$, by J. L. Snoek, Physica III, No. 6, June, 1936, page 463.). To this system is added, oxides of various bivalent metals in order to modify the properties of the basic ferrospinel system. The foregoing data is sufficiently broad to show that the water soaking operation disclosed improves the squareness of the ferrospinel system regardless of the addition of numerous additives and regardless of variations of the sintering treatment employed to vary the coercivity of the resulting body.

While the invention has been particularly shown and described with reference to specific embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. A method of producing a ferrospinel body of the rectangular hysteresis loop type which improves the squareness of the hysteresis characteristic comprising the steps of preparing an intimate mixture of metallic oxides including ferric oxide and at least one bivalent oxide, forming a molded compressed body from said mixture, then soaking said molded body in water and thereafter placing the wet body in a furnace and sintering the body at a temperature sufficient to produce a ferrospinel body.

2. The method of claim 1 in which said molded body is soaked for a period of approximately 3 to 50 minutes.

3. The method of claim 1 in which said molded body is soaked for a period of approximately 5 to 30 minutes.

4. The method of claim 1 wherein the mixture of metallic oxides includes an oxide of manganese.

5. The method of claim 4 in which said molded body is soaked for a period of approximately 3 to 50 minutes.

6. The method of claim 4 in which said molded body is soaked for a period of approximately 5 to 30 minutes.

7. A method of producing a ferrospinel body of the rectangular hysteresis loop type which improves the squareness of the hysteresis characteristic comprising the steps of preparing an intimate mixture of metallic oxides including ferric oxide and at least one bivalent oxide, adding a binder to said mixture, forming a molded compressed body from said mixture and binder, preheating said molded body to a temperature sufficient to drive off the binder, then soaking said molded body in water and thereafter placing the wet body in a furnace and sintering the body at a temperature sufficient to produce a ferrospinel body.

8. The method of claim 7 wherein the molded body is soaked for a period of between about 3 minutes and 50 minutes.

9. The method of claim 7 wherein the molded body is soaked for a period of between about 5 minutes and 30 minutes.

10. The method of producing a ferrospinel body having a substantially square hysteresis characteristic comprising, preparing an intimate mixture of metallic oxides including about 55 mol percent of MnO, about 5 mol percent of CuO and about 40 mol percent of Fe_2O_3, adding a binder to said mixture to facilitate molding, forming a molded compressed body of said mixture and binder, heating said molded body to a temperature sufficient to drive off the binder, then soaking said molded body in water and thereafter placing said wet body in a furnace and sintering the body at a temperature between about 1100° C. and about 1500° C.

11. The method of claim 10 wherein said molded body is soaked in water for a period of about 15 minutes.

12. The method of producing a ferrospinel body having a substantially square hysteresis characteristic comprising, preparing an intimate mixture of metallic oxides including about 38 mol percent of Fe_2O_3, about 57 mol percent of MnO, about 2 mol percent of NiO, and about 3 mol percent of CrO, adding a binder to said mixture to facilitate molding, forming a molded compressed body of said mixture and binder, heating said molded body to a temperature sufficient to drive off the binder, then soaking said molded body in water and thereafter placing said wet body in a furnace and sintering the body at a temperature between about 1100° C. and about 1500° C.

13. The method of claim 12 wherein said molded body is soaked in water for a period of about 15 minutes.

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