FIG. 1

Coercive force (Hc) in Oersteds vs. Calcium weight percent.

FIG. 2

Magnetic induction (B) in Gauss vs. Field strength (H) in Oersteds.

FIG. 3

Magnetic induction (B) in Gauss vs. Field strength (H) in Oersteds.
FERRITE COMPOSITIONS AND METHOD OF MANUFACTURE

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This invention relates to a method for making ferrite materials having a substantially rectangular hysteresis loop characteristic and low coercive force, and further to the ferrite materials so produced.

Ferrite materials having substantially rectangular hysteresis loops and low coercive forces are well known in the art and advantageously utilized in magnetic memory devices such as that described in an article by J. A. Rajchman in the October 1953 Proceedings of the Institute of Radio Engineers, Volume 41 No. 10, pages 1407—1421, entitled “A Myriabit Magnetic Core Memory Element.”

United States Patent 2,715,109 issued August 9, 1955, to Albers-Schoenborg, describes a MnO-MgO-Fe₂O₄ ferrite system exhibiting particularly desirable hysteresis loop and coercive force characteristics. This system encompasses the compositional range of 5 to 60 mol percent MnO, 8 to 50 mol percent MgO, and 25 to 47.5 mol percent Fe₂O₃.

A lowering in the coercive force exhibited by these compositions, particularly over the compositional range 4—67 mol percent MnO, 8—55 mol percent MgO, and 25—47.5 mol percent Fe₂O₃ is realized with zinc oxide additions of up to 8 percent by weight of composition, in accordance with United States Patent 2,981,689, issued April 25, 1961 to Albers-Schoenborg.

Additions above 8 percent are strictly avoided due to the adverse effect of the zinc oxide additions on the hysteresis loop characteristic of the ferrite system.

As discussed in these patents, calcium oxide additions to these compositions over the restricted range of 0.5 to 5.0 percent by weight of composition act to further lower coercive force without significantly detracting from the rectangularity of the hysteresis loop. Additions of at least 0.5 percent are required to noticeably lower coercive force and additions above 5.0 percent sufficiently detract from the rectangular hysteresis loop characteristic so as to preclude their use.

In accordance with the instant invention, it has been determined that calcium inclusions in the above-identified manganese-manganese ferrite compositions in amounts smaller than hereofore utilized by the art result in significantly lower coercive force values when the calcium is added by the method of the invention.

More particularly, it has been found that the introduction of calcium during the ferrite-forming process in the form of a soluble salt having a solubility with respect to calcium of at least one gram of calcium per 100 cc. of water permits the attaining or minimum coercive force values while maintaining rectangularity of the hysteresis loop.

A low coercive force, rectangular hysteresis loop composition result from calcium additions made by this method over the calcium inclusion range of 0.075 to 0.30 percent by weight of the composition.

A more complete understanding of the invention may be gained from the following description in conjunction with the accompanying drawing, in which:

FIG. 1 is a graph on coordinates of coercive force in oersteds against weight percent calcium showing the coercive force of two identical ferrite compositions containing varying amounts of calcium, the calcium being added as a carbonate to the composition depicted by curve 1 and as a soluble salt to the composition depicted by curve 2.

FIGS. 2 through 4 are graphs on coordinates of magnetic induction B in gauss against field strength H in oersteds, showing reproducibility of the actual pictures of hysteresis loops as traced on the screen of an oscilloscope of three identical ferrite compositions containing varying amounts of calcium added to the compositions during processing as a soluble salt, the ferrites being fired at a temperature of 1300° C. for 7½ hours, and

FIG. 5 is a graph on coordinates of magnetic induction B in gauss against field strength H in oersteds, showing a reproduction of an actual picture of a hysteresis loop as traced on the screen of an oscilloscope of a MnO-MgO-ZnO-Fe₂O₃ ferrite composition containing 0.2 percent by weight calcium added to the ferrite as a soluble salt, the ferrite being fired at a temperature of 1250° C. for 10 hours.

Referring more particularly to FIG. 1, depicted curve 1 shows the relationship between coercive force and calcium content of MnO-MgO-Fe₂O₃ ferrite composition in which the calcium was added as calcium carbonate. This curve is substantially identical to the one resulting when calcium is added as calcium oxide. Commensurate with the art, for example United States Patent 2,715,109, calcium hexacarbonate has been utilized in the ferrite-forming process as either the oxide or carbonate.

Curve 2 of FIG. 1 depicts the relationship between coercive force and calcium content of the same composition as curve 1. However, in accordance with the invention, calcium was added as a soluble salt, in this instance calcium acetate. This curve is exemplary of other soluble calcium salts, such as calcium benzoate, having a solubility with respect to calcium of at least one gram of calcium per 100 cc. of water.

The significant decrease in coercive force realized by calcium additions in the form of soluble salts is illustrated by a comparison of curves 1 and 2. As shown by curve 2, calcium additions in the form of soluble salts result in a decrease in coercive force for 0.1 percent calcium, in a decrease in coercive force from 1.04 to 0.67 oersteds. Increasingly larger additions result in a correspondingly sharp decrease in coercive force until, for example, a coercive force of 0.225 oersted is achieved for calcium additions of 0.25 percent by weight. Although not plotted, further decreases in coercive force result from even larger additions.

In contrast, as shown by curve 1, calcium additions in the form of oxides or carbonates result, for 0.1 percent calcium, in a decrease in coercive force from 1.04 oersteds to 0.773 oersted. Thereafter, further calcium additions cause the coercive force to increase to an essentially stable value of 1.0 to 1.04 oersteds over the calcium inclusive range of 0.25 to 0.72 percent by weight of composition. A decrease to 0.71 oersted is then experienced over the calcium inclusion range of 0.8 to 1.0 percent. Although not plotted, further calcium additions up to 1.6 percent decrease the coercive force to 0.65 oersted.

Both ferrite compositions depicted by curves 1 and 2 of FIG. 1 have the same basic ferrite composition: 32.1 mol percent magnesium oxide, 25 mol percent manganese oxide, and 42.9 mol percent ferric oxide. Both compositions were processed under identical conditions including a firing at 1300° C. for 12.5 hours. The data exemplified by curves 1 and 2 of FIG. 1 is exemplary of all magnesium-manganese ferrite compositions disclosed in United States Patents 2,715,109 and 2,981,689.

FIGS. 2 through 4 show the hysteresis loops associated with a 32.1 mol percent magnesium oxide, 25 mol percent manganese oxide, and 42.9 mol percent ferric oxide ferrite composition containing 0, 0.1, and 0.25 percent by weight calcium, respectively, the calcium being added
The 0.1 percent calcium-containing composition, in common with the calcium-free compositions, exhibits 20 rectangular faces and sharp corners. The 0.25 percent calcium-containing composition, while also exhibiting good rectangularity, has somewhat rounded corners. Although not shown in the figures, it has been found that the corners of the hysteresis loops of compositions containing an amount of calcium in excess of 0.30 percent are too rounded to satisfy the requirements of a rectangular loop ferrite.

Commensurate with the dual objectives of forming a low coercive force, rectangular hysteresis loop ferrite composition, the data discussed in conjunction with the figures dictates the calcium content for the previously described ferrite compositions of 0.075 to 0.30 percent calcium by weight of the composition. Calcium inclusions greater than 0.30 percent adversely affect the rectangularity of the hysteresis loop, with inclusions less than 0.075 percent being too small to sufficiently minimize coercive force. In these calculations, a preferred calcium content range is 0.13 to 0.30 percent by weight, with an optimum range being 0.20 to 0.25 percent.

FIG. 5 shows the hysteresis loop associated with a 20 mol percent magnesium oxide, 23.1 mol percent manganese oxide, 39.5 mol percent ferric oxide, and 17.4 mol percent zinc oxide ferrite composition containing 0.06 percent by weight calcium. As shown, the zinc-containing composition exhibits good rectangularity and the corners of the curve, while being somewhat rounded, are sufficiently sharp to satisfy the requirements of a rectangular hysteresis loop ferrite. Zinc oxide additions in excess of 18 mol percent sufficiently detract from the rectangularity of the loop as to preclude their inclusion in the magnesium-manganese ferrite compositions disclosed in United States Patents 2,715,109 and 2,981,689.

As evidenced by FIG. 5, therefore, the calcium-containing compositions of the invention permit the beneficial inclusion of zinc oxide in amounts up to 18 mol percent (14 percent by weight of composition). In contrast, United States Patent 2,981,689 precludes such additions in amounts greater than 8 percent by weight due to their adverse effect on the rectangularity of the loop. With the exception that calcium is initially present as a soluble salt, the ferrite-forming process of the invention is otherwise conventional and, as such understood by the art. Commensurate with the art, such processing includes forming a slurry of the desired components and then drying the slurry and recrystallizing the resulting solids to achieve a nearly uniform size. The mixture has the hysteresis loop depicted by FIG. 5 of the drawing and a coercive force of 0.67 oersted.

Example 2

54.7 grams magnesium carbonate, 58.0 grams manganese carbonate, 138.1 grams ferric oxide, and 0.79 gram calcium acetate were dry mixed. The mixed ingredients were then ground into an Eppenbach Homo-Mixer and enough distilled water was added thereto to form a slurry. The slurry was then dried in a heated planetary mixer. The dry powder cake thus obtained was then calcined in a vacuum at a temperature of 700° C. for 16 hours. After calcining, the mixture was ball-milled in carbon tetrachloride for 16 hours. A ten percent by weight addition of Halowax to serve as a binder was introduced during ball milling. After ball milling, the solvent was substantially removed by drying the mixture in a heated planetary mixer. The material was then granulated by passing it through a #20 United States standard screen mesh and then further dried for six hours in a vacuum at a temperature of 45° C. to remove the last traces of the solvent. The material was then heated into a ring having the dimensions 0.50 inch O.D. and 0.35 inch I.D. under a pressure of 50,000 pounds per square inch. After shaping, the ring was deaerated by bringing it to a temperature of 400° C. over a period of six hours and maintaining the 400° C. temperature for another six hours. The final firing of the ring was carried out in an oxygen atmosphere at a temperature of 1300° C. for 7.5 hours. The ring was then allowed to cool to room temperature in a nitrogen atmosphere.

The formed ring had the composition of 32.1 mol percent magnesium oxide, 25 mol percent manganese oxide, 42.9 mol percent ferric oxide, and 0.1 percent calcium by weight of the composition. The ring had the hysteresis loop depicted by FIG. 5 of the drawing and a coercive force of 0.67 oersted.
FIG. 4 of the drawing and a coercive force of 0.225 oersted.

Example 3

33.2 grams magnesium carbonate, 52.2 grams manganese carbonate, 124.1 grams ferric oxide, 27.9 grams zinc oxide, and 1.58 grams calcium acetate were dry mixed. The mixture then underwent the same processing steps described in conjunction with Example 1.

The formed ring had the composition: 20 mol percent magnesium oxide, 23.1 mol percent manganese oxide, 39.5 mol percent ferric oxide, 17.4 mol percent zinc oxide, and 0.2 percent by weight calcium. The ring had the hysteresis loop depicted by FIG. 5 of the drawing and a coercive force of 0.13 oersted.

What is claimed is:

1. A method of making a rectangular hysteresis loop ferrite composition comprising the steps of slurrying with water, drying, and calcining a mixture comprising components equivalent to 5 to 60 mol percent manganese oxide, 8 to 50 mol percent magnesium oxide, 25 to 50 mol percent ferric oxide, and containing from 0.075 to 0.30 percent calcium by weight of the mixture added as a soluble salt having a solubility with respect to calcium of at least one gram of calcium per 100 cc. of water, shaping the resultant material into the desired configuration under a pressure of 5,000 to 50,000 pounds per square inch, and firing the shaped material at a temperature of from 1200° C. to 1350° C., the said soluble salt being of such nature as to yield calcium oxide during the said method.

2. The method in accordance with claim 1 wherein said mixture contains from 0.13 to 0.30 percent calcium added as calcium acetate.

3. The method in accordance with claim 2 wherein said mixture contains from 0.20 to 0.25 percent calcium.

4. A method of making a rectangular hysteresis loop ferrite composition comprising the steps of slurrying with water, drying, and calcining a mixture comprising components equivalent to:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO</td>
<td>4 to 67</td>
</tr>
<tr>
<td>MgO</td>
<td>8 to 55</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>25 to 47.5</td>
</tr>
<tr>
<td>ZnO</td>
<td>0 to 18</td>
</tr>
</tbody>
</table>

and from 0.075 to 0.30 percent calcium by weight of the mixture added as a soluble salt having a solubility with respect to calcium of at least one gram of calcium per 100 cc. of water, shaping the resultant material into the desired configuration under a pressure of 5,000 to 50,000 pounds per square inch, and firing the shaped material at a temperature of from 1200° C. to 1350° C., the said soluble salt being of such nature as to yield calcium oxide during the said method.

5. The method in accordance with claim 4 wherein said mixture contains from 0.13 to 0.30 percent calcium added as calcium acetate.

6. The method in accordance with claim 5 wherein said mixture contains from 0.20 to 0.25 percent calcium.


References Cited by the Examiner

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