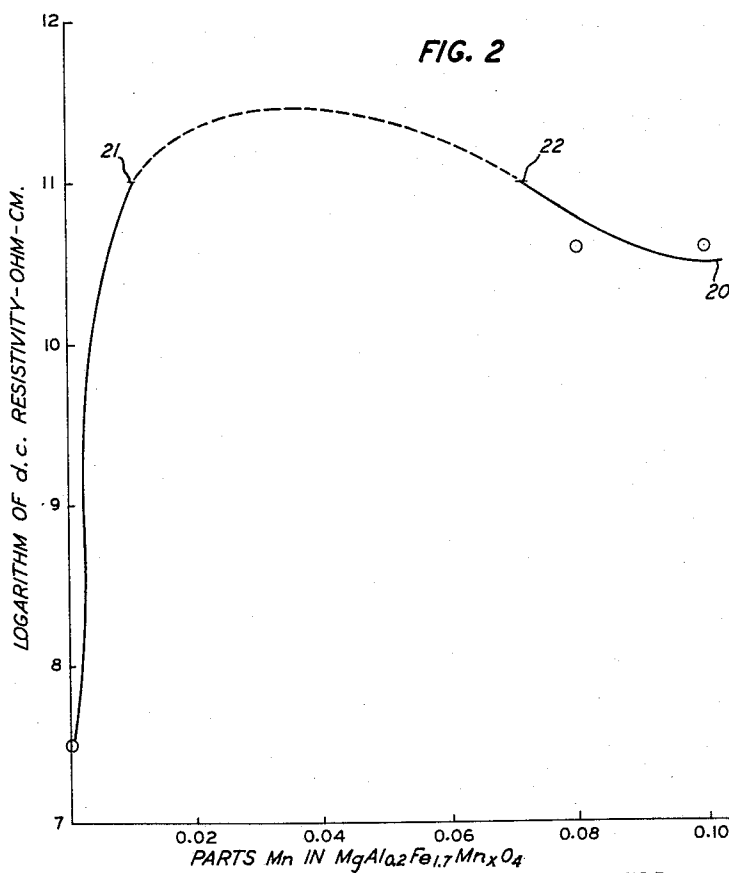
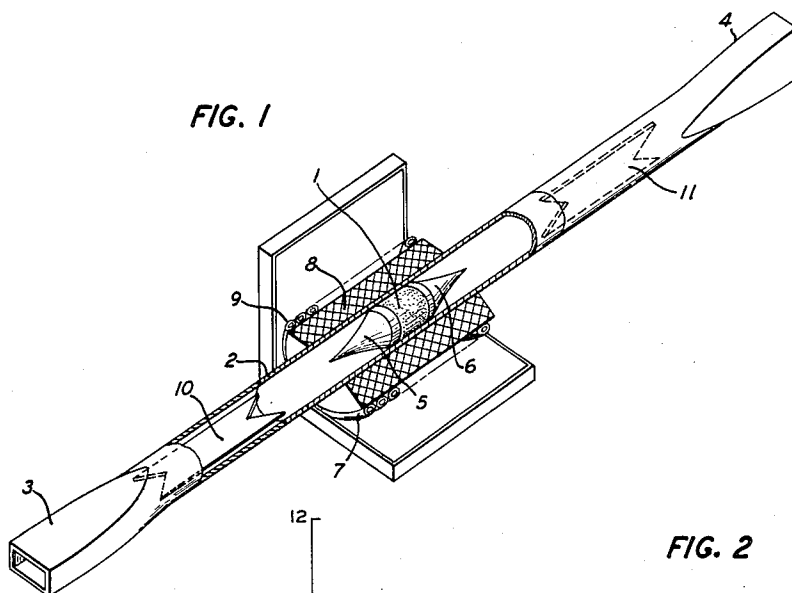


Feb. 27, 1962

LE GRAND G. VAN UITERT  
MAGNESIUM FERRITE CONTAINING ALUMINUM  
AND METHOD OF MAKING SAME  
Filed Aug. 17, 1956

3,023,165



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3,023,165

## MAGNESIUM FERRITE CONTAINING ALUMINUM AND METHOD OF MAKING SAME

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Filed Aug. 17, 1956, Ser. No. 604,740

6 Claims. (Cl. 252—62.5)

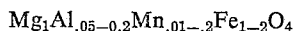
This invention relates to ferromagnetic materials of the magnesium manganese aluminum ferrite system, to methods of making these compositions and to microwave apparatus utilizing these materials.

This application is a continuation-in-part of application Serial No. 412,962, now abandoned, filed February 26, 1954 and all claims herein contained are based on the description contained in the former application.

Since the discovery of the Faraday effect in ferrites at microwave frequencies and the development of the microwave gyrator and associated circuit elements utilizing ferrites, an extensive search has been made for ferrites which are essentially transparent to microwave radiation when they are subjected to a magnetic field which is sufficient to take them near to magnetic saturation. In the early stages of this work, several materials showing high Faraday rotation and low loss for frequencies upwards of 7,000 megacycles were found. However, up to the time of my invention claimed in the said application Serial No. 412,962, now abandoned, no ferrites satisfying these conditions in the frequency range from about 3,000 to 7,000 megacycles had been found so that circuits designed for use in this, one of the earliest microwave carried bands to be allotted for commercial use, had included no ferrite elements.

I have discovered a new series of ferrite materials which show very desirable properties for use in ferrite elements intended for use in this lower microwave region. These materials are magnesium ferrites modified by the substitution of aluminum for part of the iron and in which conductivity losses are further suppressed by the addition of manganese, and in some compositions, additionally, by employing less than stoichiometric amounts of iron so as to produce iron deficient ferrites. This specification contains a complete description of these new materials together with a disclosure of the critical processing conditions which must be adhered to if materials having the properties described are to be produced. The materials described are of special interest for use in microwave gyrators, polarization circulators and other circuit elements depending for their operation on Faraday rotation at microwave frequencies of from 3,000 megacycles up to 7,000 megacycles, and in other types of apparatus designed for bringing about phase shifting and field shifting such, for example, as the transverse field phase shifter. The described materials may also find use, for example, in traveling wave tubes and resonant cavities. A good description of the microwave gyrator, which may be an element in a wave guide, and of some other elements dependent for their operation upon Faraday rotation is to be found in an article by C. L. Hogan in the Bell System Technical Journal, volume 31, at page 1 et seq. A more general description of Faraday effect at microwave frequencies by the same author appears in Reviews of Modern Physics, volume 25, pages 253 to 263.

The general formula of the compositions described and claimed herein is:



in which general formula the maximum amount of manganese present is 10 atomic percent of the amount of iron.

As an aid in teaching the described invention, two figures are presented as follows:

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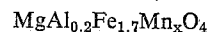
FIG. 1 is a perspective view of a wave guide containing a ferrite element which may function as a gyrator and is taken from the figure appearing on page 18 of the Bell System Technical Journal article to which reference is made above; and

FIG. 2 is a plotted curve based on experimental results designed to indicate the variation in the resistivity of the final ferrite material with a variation in the amount of manganese used in composition included in the general formula set forth above.

Referring again to FIG. 1 there is depicted a Faraday rotation device comprising a ferrite element 1 composed of any of the materials considered later herein placed in a circular wave guide 2 which is about 12 inches long. Two rectangular wave guides 3 and 4 are connected with circular wave guide 2 as shown. That portion of circular wave guide 2 containing ferrite element 1 which element is butted to tapered portions 5 and 6 which may consist of a dielectric material such as polystyrene is encompassed by structure 7 comprising electrical winding 8 and cooling coil 9. Electrical winding 8 is energized by an electrical source not shown to produce a horizontal magnetic field in the region of ferrite magnetic element 1, the said field being sufficient to take element 1 near to magnetic saturation. Radial veins 10 and 11 are inserted for the purpose of absorbing reflections. For the device shown vein 10 is so placed as to absorb horizontally polarized waves while radial vein 11 is so positioned to absorb vertically polarized waves. Tapered transitions 5 and 6 are intended to reduce reflections so absorbed.

A complete description of the mode of operation of wave guide apparatus such as that depicted in FIG. 1 is beyond the scope of this description. The principle of operation of such an element may be obtained from the Bell System Technical Journal article to which reference is made above.

Referring again to FIG. 2, curve 20, on coordinates of logarithm of D.C. resistivity in ohm-centimeters on the abscissa and parts of manganese in the formula



on the ordinate, which composition falls within the general formula above, indicates the effect of a variation in the amount of manganese in an otherwise fixed composition on the resistivity of the ferrite. The curve so shown is based on actual experimental observations on materials which were produced in accordance with the procedure outlined in Example 2 herein.

The data plotted on this curve is representative of resistivity characteristics for six compositions in accordance with the formulation set forth on the figure and containing manganese in the following amounts: 0, 0.02, 0.04, 0.06, 0.08 and 0.1 parts. The dotted portion 21—22 of the curve is representative of that part of the curve corresponding with resistivity measurements made on three compositions containing 0.02, 0.04 and 0.06 parts of manganese. Current passing through these samples was however too low to be susceptible to accurate measurement on the instrument used. This portion of the curve is considered to be extremely conservative in that from the known accuracy of the instrument the actual resistivity values for these three materials are well above the values represented by this portion of the curve.

In making up the samples for the resistivity data plotted on FIG. 2, the procedures outlined in Example 2 were followed. After the samples were fired, they were in the form of discs of a diameter of approximately one inch. The discs were then machined flat on both circular surfaces to a thickness of 50 mils. One flat area contact covering the entire circular area of the disc was made to each of the two circular areas, a D.C. voltage potential of 18 volts was applied across the two area contacts,

the current passing through the disc was measured, and the resistivity was calculated.

The efficiency of a ferrite element for use in microwave apparatus such, for example, as the wave guide structure of FIG. 1 is generally measured in terms of "insertion loss," which is simply the loss in power resulting from the insertion of such an element in such a wave guide structure. Such insertion loss varies inversely with the resistivity of the ferrite so that from FIG. 2 it is seen that adding manganese to the magnesium aluminum ferrite results in decreasing the insertion loss. Although changing ferrite composition by varying the amount of manganese may result in small changes in the characteristics of the end product other than resistivity, such changes over the composition range indicated are minor and of no consequence when compared with the magnitude of change in the resistivity value indicated.

Providing therefore that the firing conditions and other conditions of treatment of the materials over the range indicated are identical, and provided the conditions of application of the elements constructed of these materials are identical, it is seen that a reduction in insertion loss necessarily results upon the addition of manganese to a magnesium aluminum ferrite.

A general index of the quality of a ferrite for microwave applications depending upon Faraday rotation is the magnitude of the rotation of the plane of polarization per unit absorption of energy from the transmitted wave. Typical values of this index for the best commercially available ferrites are 400 to 500 degrees rotation per decibel (db) of energy lost in a wave guide at 9,000 megacycles and, until the development described herein, about 10 to 20 degrees per db at 4,000 megacycles. Prior to my work it was thought that the way to increase this index in the microwave frequency range of about 4,000 megacycles was to develop materials having higher intrinsic magnetic saturation moments so that the Faraday rotation per unit volume of ferrite would be increased. My studies, however, have indicated that extension of this principle to the development of materials for use in this frequency range is not justified since an increase in the magnetic moment of such materials results in a corresponding proportionally greater increase in loss so that the resultant index as herein defined is actually lower. In fact, a study of the loss mechanisms at the microwave frequencies hereunder studied has led to the conclusion that the solution to the problem is the production of a ferrite with a much lower intrinsic saturation moment than that of most commercially available ferrites combined, however, with low dielectric loss. These studies have led to the materials herein described which, to date, have given measured figures of merit of greater than 500 degrees per db at 4,000 megacycles.

The next section of this specification is an outline of the procedural steps which are to be followed in carrying out the teachings of this invention. Following this section and accompanying discussion relating to the effect of varying certain conditions of treatment on the final characteristics of the material, there are set forth two numbered examples of procedural steps which were followed in preparing several materials falling within the scope of the general formula set forth above.

#### OUTLINE OF MANUFACTURING PROCEDURE

The compositions of this invention are of the general formula



in which general formula the maximum amount of manganese present is 10 atomic percent of the amount of iron. In setting forth a procedure designed toward obtaining a desired composition within this general formula, compounds which are in themselves, or which will upon calcining yield, oxides of the metallic elements to be contained in the final composition are selected.

The amounts of each of the components are determined in accordance with the composition which is desired. Suitable starting materials include the oxides of all of the elements with the single exception of aluminum oxide, the desirable properties attributed to the ferrites of this invention being obtainable only by the use of aluminum hydroxide or by the use of compounds which by in situ reaction may be caused to result in aluminum hydroxide. An example of such an in situ reaction is the use of aluminum chloride which in the presence of the basic magnesium mixture results in the formation of aluminum hydroxide.

In connection with the form in which the aluminum addition is made, it is to be expected that the use of the hydroxide will result in a very fine dispersion of aluminum oxide. Since, however, experiments have established that the use of even the finest grade of aluminum oxide obtainable does not result in ferrite materials having the desirable microwave characteristics herein described, the advantage of the hydroxide over the oxide is clearly not entirely attributable to a finer particle size of aluminum being realized by its use.

Magnesium is added in the form of magnesium carbonate or other compound which upon oxidation during calcining results in magnesium oxide a preference existing for the carbonate. Manganese is also added in the form of the carbonate or other material which will yield the oxide upon calcining.

The following tables indicate the amounts of starting materials to be used in obtaining the ferrite materials of this invention. Both weight and molar proportions of starting materials are indicated. Table I indicates proportions of suitable starting materials. The proportions of Table II are in terms of oxides.

Table I

| Material                             | Weight     | Mols    |
|--------------------------------------|------------|---------|
| MgCO <sub>3</sub> .....              | 100        | 1       |
| Fe <sub>2</sub> O <sub>3</sub> ..... | 95-190     | 0.5-1   |
| Al(OH) <sub>3</sub> .....            | 4-19       | 0.05-.2 |
| MnCO <sub>3</sub> .....              | 1.42-28.40 | .01-.2  |

Table II

| Material                             | Weight  | Mols     |
|--------------------------------------|---------|----------|
| MgO.....                             | 100     | 1        |
| Fe <sub>2</sub> O <sub>3</sub> ..... | 200-400 | 0.5-1    |
| Al <sub>2</sub> O <sub>3</sub> ..... | 6-25    | 0.025-.1 |
| MnO <sub>2</sub> .....               | 2.5-50  | .01-.2   |

The starting materials are mixed in a paste mixer. This mixing step may be carried out in a water slurry, but due to the slight solubility of magnesium carbonate or magnesium oxide in water, it has been found preferable in certain instances to use a non-aqueous solution, such, for example, as acetone, carbon tetrachloride, or ethanol. Where a combustible solution is used, mixing is preferably carried out in a ball mill or other enclosed equipment in which the fire hazard is minimized. Although the mixing step can be carried out dry, the result will be a cake rather than an intimate mixture of powders.

The mixture is then dried either by filtering if a water slurry is used or by evaporation if a non-aqueous solvent is used. Although it is not necessary to remove all of the liquid from the mixture, if an irritating solvent such as carbon tetrachloride is used it is preferable to dry the mixture completely to protect the operator. The evaporation step may be carried out in air.

The mixture is then calcined for about 12 hours in air at a temperature of from 200° C. to 400° C. below the final firing temperature. Since, as will be discussed, for most operations final firing is carried out at from 1200° C. to 1400° C., calcining may generally be carried out at from about 800° C. to about 1200° C.

The mixture is now broken up in a ball mill for a period of about 15 hours in a liquid such as carbon tetrachloride, ethanol, acetone or water. Some time during this grinding process, either at the start or any time later, a binder such as Halowax (chlorinated naphthalene), opal wax, or paraffin is added. This binder, which is either dissolved by the carbon tetrachloride or other grinding medium during the milling step or is added in the form of a solution in a volatile solvent, acts as a lubricant during the pressing procedure.

The carbon tetrachloride or other non-aqueous solvent is removed by heating while providing for removal of the vaporous solvent. Stirring during this solvent removal step, for example at from three to four revolutions per second, assures uniform dispersion.

The resultant waxy mixture is passed through a screen in order to obtain uniform granules. A 20-mesh screen has been found to be satisfactory for this purpose.

The particles are now put in a vacuum oven so as to remove the last traces of solvent. The oven is maintained at a temperature of from 40° C. to 50° C. or higher, the temperature however being kept below the volatilization point of the wax. Operation of the oven for a period of from 4 to 12 hours is sufficient to remove virtually all the solvent. Although this solvent removal step can be carried out in any ordinary oven, there must be a provision made for the removal of the solvent.

The mixture is next pressed at a pressure of from 30,000 pounds per square inch to 60,000 pounds per square inch, depending on the desired results. The lower the pressure the more inhomogeneous the resultant material and, consequently, the less sharp the ferromagnetic resonant peak. For the general purposes outlined in this disclosure, a pressure of 50,000 pounds per square inch has been found to be suitable. The shape into which the material is pressed is not critical and depends only on the shape desired, the usual bar, slab, disc or ring forms being used. Pressing may be carried out at room temperature.

The wax having served its function as a lubricant during the pressing process, the pressed pieces are dewaxed in an oven according to a temperature-time program. If a schedule similar to the one set forth below is followed homogeneous material results.

| Time:        | Temperature, ° C. |
|--------------|-------------------|
| 6 hours----- | 100               |
| 3 hours----- | 150               |
| 3 hours----- | 200               |
| 3 hours----- | 250               |
| 3 hours----- | 300               |
| 6 hours----- | 400               |

Since the boiling point of the waxes used is in the range of 75° C., most of the wax comes out during the 100° C. heating step. Heating to succeeding higher temperatures results in the removal of that portion of the wax that polymerizes as the heating is carried out. Although other heating schedules will work satisfactorily, there are certain conditions which must be adhered to if most of the wax is to be removed without damage to the pressed bar. For example, bringing the body up to a temperature very much in excess of the boiling point of the wax quickly will tend to cause cracking and may produce holes in the pressed body.

Heating the body to temperatures in excess of about 500° C. results in the crystallization of a large amount of the material so that the final product after firing will be inhomogeneous and less dense. In connection with the dewaxing step, it is understood that the desired product is homogeneous and has a narrow resonance peak, such material being particularly useful in the microwave range of from 3,000 to 7,000 megacycles. Since, for operation above this range a higher rotation per db may be realized with less dense material, there may be a slight advantage gained by carrying the dewaxing schedule to higher temperatures.

Final firing is carried out in any conventional furnace which can be heated to the range of from 1300° C. to 1400° C. as for example, in a Globar, platinum, or gas type furnace. Final firing is carried out in an atmosphere of air or oxygen. For microwave applications not dependent on broad resonance peaks, for example, such as Faraday rotation applications in the 3,000-megacycle to 7,000-megacycle band, it is desirable to raise the temperature of the mix to its ultimate value of at least about 1200° C. and preferably 1300° C. or higher as quickly as possible. Such a procedure produces materials having much higher densities than materials brought to the ultimate temperature slowly. Materials so produced may have densities of from 2 to 4½ grams per cubic centimeter. The density of the end product may be further increased by the introduction of water prior to or during the final firing procedure. Although water vapor may be introduced during firing, it may have a deleterious effect on the heating element of the furnace if an electrical element is used. It is therefore usually found preferable to prehumidify the dewaxed bodies, or to ball mill in water after calcining.

As has been indicated, characteristics of the final product depend on composition and processing conditions. In general, highly homogeneous materials are to be preferred for application in the 3,000-megacycle to 7,000-megacycle band. Homogeneity, in general, increases with density, which may be increased by increasing moisture content during firing, increasing firing temperature and the rate of approach to the firing temperature, and by increasing the iron deficiency. Manganese addition probably has a "mineralizing" action similar to that of water so that the density of the final material will probably show a slight increase with increasing manganese addition. Since for frequencies above 7,000 megacycles less dense materials are generally preferred, it may be to advantage to utilize lower firing temperatures, to approach these firing temperatures more slowly and to introduce no water prior to or during final firing.

In compositions included in the general formula above, it is important to have an iron deficiency to suppress the formation of divalent metal ions which have the effect of increasing the conductivity and, therefore, of increasing the eddy current loss of the material. In general, iron deficiencies of from 5 percent to 10 percent have been found to greatly improve the loss characteristics of the final material, although iron deficiencies of as little as 1 percent or less have an ascertainable effect. Where it is desired to obtain or where there is no objection to producing a heterogeneous material, conductivity loss may be further decreased by increasing the iron deficiency to values as great as 66 percent although, in general, little advantage is gained by going above 25 percent. For the purpose of this description, iron deficiency is given in terms of the amount of metal ion which will have to be added to ionically balance four oxygen atoms, or for the general formula above

$$\text{percent iron deficiency} = \left[ \frac{2Mg - (Fe + Mn + Al)}{2} \right] \times 100$$

As has been discussed, in general, although increasing the magnetic saturation moment of the ferrite has the effect of increasing the Faraday rotation for operation in the frequency range of from 3,000 megacycles to 7,000 megacycles, the losses are increased out of proportion to the improvement in Faraday rotation so that the resultant figure of merit is actually less. Reducing the saturation moment of the ferrite has the effect of increasing the figure of merit so that the number of degrees of Faraday rotation per db loss is increased. It should be noted that the critical saturation moment is that of the individual crystallites themselves, the losses not being reduced by virtue of air gap or other dilution effect which give an apparent lower saturation moment. For use in the frequency spectrum from 3,000 megacycles up to 7,000 or

8,000 megacycles, the material should have an intrinsic saturation, that is, saturation moment of the individual crystallites, of the order of 1,800 gaussess or less depending on the exact frequency in which it is intended to use the materials. Since at 4,000 megacycles the initial loss peak is still present in a material having an intrinsic saturation of about 1,800 gaussess, ideally, for operation at this frequency, the ferrite should have a saturation moment of less than 1,800 gaussess. By use of the processes herein described, ferrites having intrinsic saturation moments of 800 gaussess and lower have been produced.

As the frequency of operation goes up it is permissible and generally preferable to use materials having higher saturation moments since at higher frequencies the contributions to loss from the initial loss peak for a given ferrite rod decrease and may be eliminated. Also the higher the saturation of the material the smaller the rod that may be used. However, up to 7,000 or 8,000 megacycles, the number of degrees of Faraday rotation per db loss may still be increased by adding aluminum to lower the saturation. For such uses ferrites produced in accordance with this disclosure in which insertion losses have been minimized by the introduction of small amounts of manganese and iron deficiency are useful. Ferrites containing .1 atom of aluminum and having intrinsic saturation moments of the order of 1800 gaussess show excellent properties in this higher range of frequencies. Above 8,000 megacycles where it is desirable to use materials having still higher saturation moments, the addition of aluminum is disadvantageous.

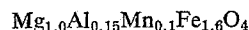
It should be especially noted that all of the desirable properties attributed to magnesium-manganese-aluminum ferrites produced in accordance with this invention are obtained only by the use of aluminum in the form of the hydroxide. Similar effects may be achieved by creating forms of hydrated alumina by in situ reactions such as by adding aluminum chloride to the basic magnesium mix. The uniform intrinsic low saturation moment materials herein described will not be obtained if the aluminum addition is made in the form of the oxide.

The following examples are descriptions of the steps followed in producing several compositions within the range of the general formula. In Example 1 the final composition is  $Mg_{1.6}Al_{0.15}Mn_{0.1}Fe_{1.6}O_4$ . Example 2 relates to the production of the six compositions on which resistivity measurements were made and plotted to produce the curve of FIG. 2. All but sample A of these six compositions is within the scope of the general formula. Example A, which contains no manganese was produced for the purpose of obtaining a reference point.

#### EXAMPLE 1

A mixture of 656 grams of magnesium carbonate, 96.6 grams of aluminum hydroxide, 985 grams of ferric oxide and 85.0 grams of manganese carbonate was prepared by water mixing in a paste mixer. Following this, the slurry was filtered and dried overnight in an oven maintained at a temperature of 110° C. The filter cake was granulated and calcined in air at 900° C. for 15 hours after which the calcined material was ball-milled for 15 hours in carbon tetrachloride during which milling procedure 200 grams of Halowax were added. The material was taken to incipient dryness by stirring in a paste mixer equipped with a heating mantle and an air-blowing ring to evaporate the carbon tetrachloride. The powder was granulated by passage through a 20-mesh screen and was dried in a vacuum oven maintained at 45° C. overnight. The final powder was pressed at 30,000 pounds per square inch into two bar-shaped bodies of dimensions  $\frac{5}{8}$ " x  $\frac{5}{8}$ " x  $3\frac{1}{2}$ ". The bars were next dewaxed by placing in a tray covered with asbestos paper in a furnace which was maintained at 100° C. for 6 hours, 150° C. for 3 hours, 200° C. for 3 hours, 250° C. for 3 hours, 300° C. for 3 hours and finally 400° C. for 6 hours. The dewaxed bars were then fired in a Global-type furnace

at 1365° C. in dry air for 10 hours. One of the bars was machined to a cylinder having a diameter of 0.430 inch and a length of 3 inches. When placed in a round 2-inch wave guide section the end product showed a Faraday rotation 52 degrees for a measured insertion loss of considerably less than 0.1 db at 4,000 megacycles which is equivalent to a figure of merit of greater than 500 degrees per db. This ferrite of composition



had a calculated density of 3.8, an iron deficiency of

$$\left[ \frac{2 - (1.6 + .1 + .15)}{2} \right] 100 = 7.5 \text{ percent}$$

and an intrinsic saturation moment of 1600 gauss.

#### EXAMPLE 2

A mixture of 843 grams of magnesium carbonate ( $MgCO_3$ ), 156 grams of aluminum hydroxide ( $Al(OH)_3$ ), 1360 grams of ferric oxide ( $Fe_2O_3$ ), and an amount of manganese carbonate ( $MnCO_3$ ) set forth below was prepared by water mixing in a paste mixer. Following this, the slurry was filtered and dried overnight in an oven maintained at a temperature of 110° C. The filter cake was granulated and calcined in air at 900° C. for 15 hours after which the calcined material was ball-milled for 15 hours in carbon tetrachloride during which milling procedure 200 grams of Halowax were added. The material was taken to incipient dryness by stirring in a paste mixer equipped with a heating mantle and an air-blowing ring to evaporate the carbon tetrachloride. The powder was granulated by passing through a 20-mesh screen and was dried in a vacuum oven maintained at 45° C. overnight. The final powder was pressed at 30,000 pounds per square inch into a disc having a diameter of 1 inch and a thickness of approximately 50 mils. The disc was next dewaxed by placing in a furnace, the temperature of which was gradually raised to 400° C. in a period of 8 hours and was held at this temperature for a period of 4 hours after which the furnace was turned off and allowed to cool to room temperature. Air was blown through the furnace during the entire heating and cooling cycle. The dewaxed disc was then fired in a Global-type furnace at 1350° C. for 10 hours. During firing an oxygen flow was maintained through the furnace. The furnace was then turned off and allowed to cool to room temperature, room temperature being attained in about 24 hours.

In accordance with the above outline, six sample discs having varying manganese content were made up. The amounts of manganese carbonate ( $MnCO_3$ ) used in each of the six samples and the resultant compositions of the final products were as follows:

| Sample | Grams Mn CO <sub>3</sub> | Composition                      |
|--------|--------------------------|----------------------------------|
| A----- | 0                        | $MgAl_{0.2}Fe_{1.7}O_4$          |
| B----- | 23                       | $MgAl_{0.2}Fe_{1.7}Mn_{0.02}O_4$ |
| C----- | 46                       | $MgAl_{0.2}Fe_{1.7}Mn_{0.04}O_4$ |
| D----- | 69                       | $MgAl_{0.2}Fe_{1.7}Mn_{0.06}O_4$ |
| E----- | 92                       | $MgAl_{0.2}Fe_{1.7}Mn_{0.08}O_4$ |
| F----- | 115                      | $MgAl_{0.2}Fe_{1.7}Mn_{0.1}O_4$  |

What is claimed is:

1. The method of manufacturing a magnesium ferrite containing aluminum comprising forming an intimate mixture of magnesium oxide, ferric oxide, aluminum hydroxide and manganese dioxide in molal amounts based on one mol of magnesium oxide as follows:

from 0.5 to 1 mol ferric oxide  
from 0.05 to 0.2 mol aluminum hydroxide  
from 0.01 to 0.2 mol manganese dioxide,

but in which mixture the maximum number of mols of

manganese dioxide is 20 percent of the number of mols of ferric oxide, and firing the said mixture in an atmosphere selected from the group consisting of air and oxygen at a temperature of at least 1200° C.

2. The process of claim 1 in which the number of mols of manganese dioxide plus half the number of mols of aluminum oxide plus half the number of mols of ferric oxide is less than twice the number of mols of magnesium oxide.

3. The method of manufacturing a magnesium ferrite containing aluminum comprising forming a mixture of aluminum hydroxide and compounds which, upon calcining, result in the presence of magnesium oxide, ferric oxide and manganese dioxide in molal amounts based on one mol of magnesium oxide as follows:

from 0.5 to 1 mol ferric oxide  
from 0.025 to 0.1 mol aluminum oxide  
from 0.01 to 0.2 mol manganese dioxide,

but in which mixture the maximum number of mols of manganese dioxide is 20 percent of the number of mols of ferric oxide, calcining the said mixture in air and subsequently firing in an atmosphere selected from the group consisting of air and oxygen at a temperature of at least 1200° C., in which method the calcining is carried out in a temperature range of from about 200° C. to about 400° C. below the firing temperature.

4. A magnesium ferrite of the general composition  $Mg_{1-x}Al_{0.05-0.2}Mn_{0.01-0.2}Fe_{1-2}O_x$ , in which general formula the maximum amount of manganese present is 10 atomic percent of the amount of iron, and in which general formula the total number of atoms of aluminum, manganese and iron is numerically equal to 2 minus a maximum deviation of 10 percent based on the fraction

$$\left[ \frac{2Mg - (Fe + Mn + Al)}{2} \right] \times 100$$

and in which  $x$  is sufficient oxygen to make the composition electrically neutral produced by the process comprising forming a mixture of aluminum hydroxide and compounds which, upon calcining, result in the presence of magnesium oxide, ferric oxide and manganese dioxide, calcining the said mixture and subsequently firing the said mixture in an atmosphere selected from the group consisting of air and oxygen at a temperature of at least 1200° C.

5. A magnesium ferrite of the general composition  $Mg_{1-x}Al_{0.05-0.2}Mn_{0.01-0.2}Fe_{1-2}O_x$ , in which general formula the maximum amount of manganese present is 10 atomic percent of the amount of iron and in which general formula the total number of atoms of iron, manganese

and aluminum is less than 2 by a maximum amount of 10 percent in accordance with the fraction

$$\left[ \frac{2Mg - (Fe + Mn + Al)}{2} \right] \times 100$$

and in which  $x$  is sufficient oxygen to make the composition electrically neutral, produced by a process comprising forming a mixture of aluminum hydroxide and compounds which, upon calcining, result in the presence of magnesium oxide, ferric oxide and manganese dioxide, calcining the said mixture and subsequently firing the said mixture in an atmosphere selected from the group consisting of air and oxygen at a temperature of at least 1200° C.

6. The method of manufacturing a magnesium ferrite containing aluminum comprising forming a mixture of aluminum hydroxide, magnesium carbonate, ferric oxide and manganese carbonate in molal amounts based on one mol of magnesium carbonate as follows:

from 0.5 to 1 mol ferric oxide  
from 0.05 to 0.2 mol aluminum hydroxide  
from 0.01 to 0.2 mol manganese carbonate,

but in which mixture the maximum number of mols of manganese carbonate is 20 percent of the number of mols of ferric oxide, calcining the said mixture in air and subsequently firing in an atmosphere selected from the group consisting of air and oxygen at a temperature of at least 1200° C., in which method the calcining is carried out in a temperature range of from about 200° C. to about 400° C. below the firing temperature.

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