

Oct. 3, 1961

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3,002,929

PROCESS FOR MAKING COMPOSITE FERRITES

Filed May 1, 1956

2 Sheets-Sheet 1

FIG. 1

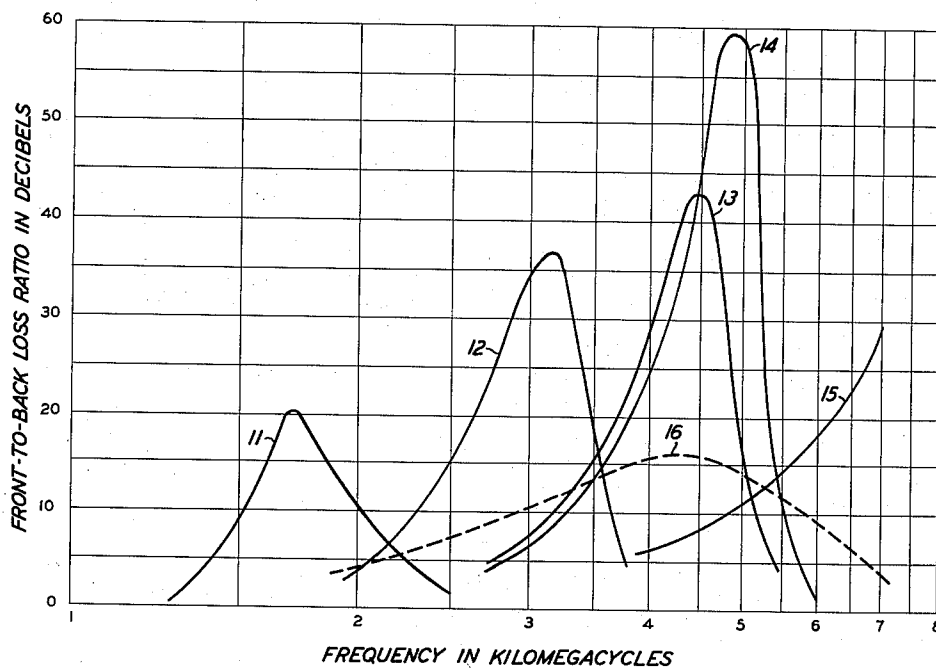
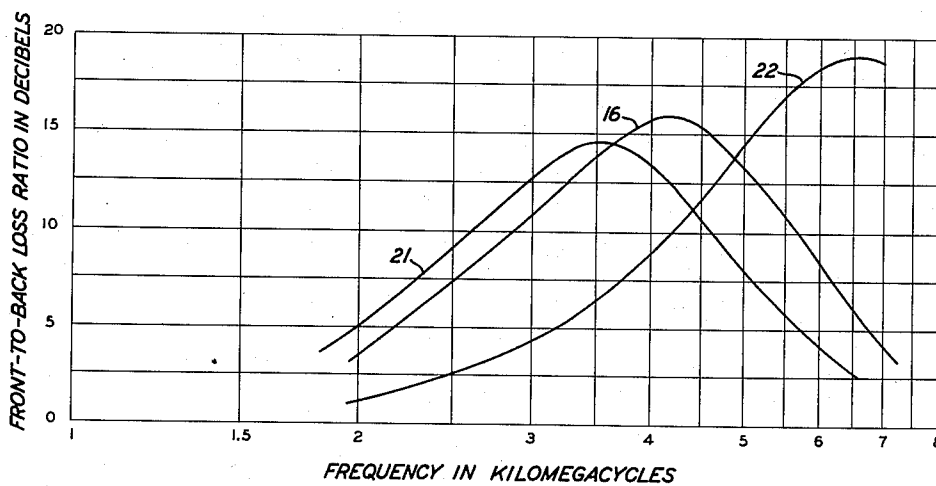


FIG. 2



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FIG. 3

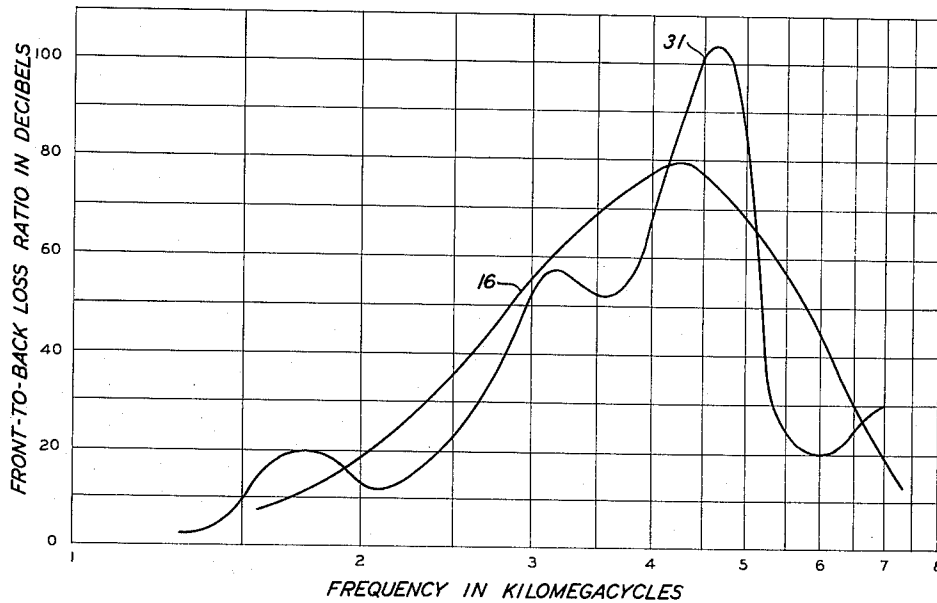
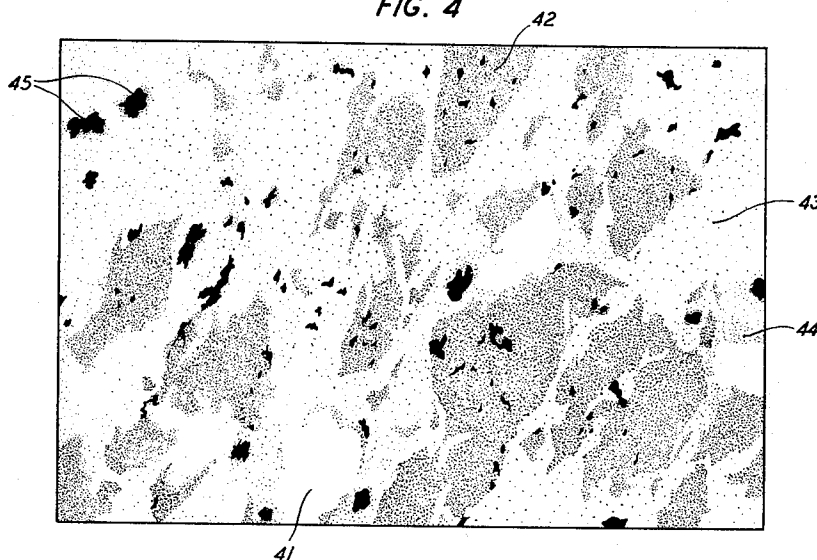


FIG. 4



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PROCESS FOR MAKING COMPOSITE FERRITES
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1 Claim. (Cl. 252—62.5)

This invention relates to methods for the preparation of inhomogeneous structures composed of magnetic ferrite materials, and to the inhomogeneous structures of magnetic ferrite materials so produced.

Ferrites are magnetic ceramic compositions of general formula MFe_2O_4 , where M may be one or more of a variety of divalent metal ions known in the art. Common deviations from the composition generalized above include partial substitution of ferric ion with other trivalent metal ions, or compounding the ferrite to be iron deficient, that is, to show a departure from the stoichiometric amount of iron dictated by the formula. Ferrite compositions of the varieties described have found many applications as core structures in inductive devices such as transformers. More recently, ferrites have become increasingly important in microwave technology.

In some microwave applications, ferrite compositions are used to absorb microwaves of a particular frequency. Microwaves whose frequencies coincide with the resonant frequency of a ferrite body through which they are passing are strongly absorbed by the ferrite. One recent device which makes use of this phenomenon is the traveling wave tube described by J. S. Cook, R. Kompfner and H. Suhl in an article in the Journal of Applied Physics, volume 26, pages 1180 through 1182, September 1955. Other devices, such as resonance isolator devices, known in the art, can also be mentioned as using ferrite compositions to absorb microwave radiation.

For a number of device applications, including the traveling wave tube mentioned above, and also in broadband resonance isolator devices, to name a second example, it is desirable to use a magnetic ferrite showing resonance absorption of microwaves over a broad band of microwave frequencies. As any one ferrite composition generally shows resonance absorption over a comparatively small band of frequencies surrounding a resonance absorption peak, the fulfillment of the concept of a single material showing broadband absorption has not previously been accomplished.

Some work has been done in the prior art to produce ferrite structures which would combine in one structure the desirable characteristics of more than one ferrite. The British patent to Philips Electrical Industries, Limited, No. 734,243, published July 27, 1955 describes ferromagnetic ferrite cores made up of assembled partial cores composed of different ferrite materials. Cores molded from layers of pulverized ferrites kept carefully separated prior to sintering are also described.

Whatever the success of these prior art composites may be for use as cores in inductive devices, their use in many microwave devices would not be indicated. A ferrite composite whose composition changes grossly from one portion of the structure to another presents a body of changing dielectric constant to an advancing microwave, for example. The velocity of the impinging wave could be altered in passing from one region within the body to another as a result of this changing dielectric constant. Similarly, in such a structure as the wave encounters different ferrite portions of different permeability, a discontinuity in the magnetic field in the structure, disruptive of the wave path, may be met. For use at microwave frequencies, a structure which is homogeneous to the micro-

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wave, though perhaps inhomogeneous when measured by other standards, is preferred.

To form a composite structure which is homogeneous to microwaves, discontinuities in composition should be no larger than about one-fifth of a wavelength and are preferably smaller. Thus for a wave of a frequency of 1000 megacycles, having a wavelength of only about 0.3 centimeter, discontinuities in structure should be no greater than 0.06 centimeter in size, preferably less. For a frequency of 100 megacycles, discontinuities in a structure, through which the microwave is passing, greater than 0.6 centimeter should be avoided, and preferably, much smaller discontinuities should be present. As the frequency of the microwave decreases, the limitations on the preferred minimum size of a discontinuity decrease in stringency.

Over the frequency band of interest in most microwave technology, said band ranging from about 100 megacycles to about 100,000 megacycles, structures in which inhomogeneities range in size from about 0.003 centimeter to about 0.5 centimeter in size still present an essentially homogeneous structure to many microwaves, especially those of lower frequency. As the frequency of the microwaves used increases, structures in which discontinuities in composition are between about 0.003 centimeter and no more than about 0.2 centimeter in size are preferred. For still higher frequency bands, the maximum size of a discontinuity is preferably kept below about 0.1 centimeter, or better, below 0.05 centimeter.

From a practical viewpoint also, layered structures such as those taught in the aforementioned British patent specification may prove awkward. Thus machining interlocking parts of a structure from different materials and fitting the parts into a whole would become more complex as desired structural shapes become more intricate. Similarly, molding shapes from layered ferrites would be more difficult, if not impossible, when structures more complicated than the simplest geometrical forms were desired. Even in molding simple forms having discretely layered portions, further, a tendency of the structure to buckle or warp on firing due to non-uniform shrinkage of the different portions of the structure has been encountered.

By the methods of the present invention, a single ferrite structure homogeneous to microwaves but with broadband resonance absorption characteristics over a desired frequency range can be quite easily fashioned. The structure, which shows uniformity and homogeneity for microwave purposes, is, however, inhomogeneous. Within the structure, a regional variation in ferrite composition can be found: each such subdivision contributes some of its individual characteristics to the whole. But by avoiding gross variations in the ferrite composition of the structure as one passes from one gross portion of the structure to another, the overall characteristics of the structure and material, including the permeability and dielectric constant, are kept uniform.

In particular, in preparing composite structures for resonance absorption of microwaves, the magnetic ferrites which are to be the components in the overall structure are selected with reference to their resonance characteristics. Materials showing resonance peaks at spaced intervals within a broad band of microwaves are included, and in this manner a broadband resonance property is imparted to the composite structure produced.

In the accompanying drawings:

FIG. 1 is a graph, the abscissa of which is frequency measured in kilomegacycles and the ordinate of which represents the front-to-back loss ratio in a ferrite structure measured in decibels, showing curves for five separate ferrites and for a composite material formed from said ferrites by the methods of the present invention;

FIG. 2 is another graph of front-to-back loss ratio in

decibels versus frequency in kilomegacycles showing three absorption curves for three different composite ferrite structures;

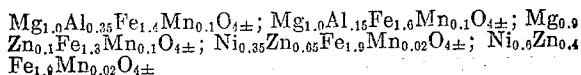
FIG. 3 is a third graph of loss ratio in decibels versus frequency in kilomegacycles showing two curves which compare the experimentally measured loss characteristics of a composite ferrite with theoretical loss characteristics predicted by an arithmetic summation of individual losses in an equivalent quantity of the component ferrites; and

FIG. 4 is a schematic view of an enlarged section of the structure of a composite body produced by the methods of the present invention.

In FIG. 1 curves 11 through 15 show graphically the resonance absorption characteristics of a representative group of ferrites, plotted as a function of frequency. As can be seen on the drawing, the ferrite represented by curve 11 peaks at approximately 1.7 kilomegacycles. Curves 12, 13 and 14, each representing the resonance losses of a different ferrite composition, peak at approximately 3.1 kilomegacycles; 4.5 kilomegacycles, and 4.9 kilomegacycles, respectively. Curve 15 represents only a portion of the resonance absorption curve of a fifth ferrite material. The absorption peak has not been reached within the frequency range of interest.

Curve 16, which is of primary interest, represents the empirical resonance absorption characteristics of a composite material compounded of equal parts by weight of the five ferrites shown in curves 11 through 15, prepared by the method disclosed herein. As can be seen from the graph in FIG. 1, substantial resonance absorption has been imparted to the composite structure over a frequency band between approximately 2 kilomegacycles and 7 kilomegacycles, with maximum absorption being shown at about 4.2 kilomegacycles. The shape of the curve of the composite can be varied, within limits, by variation in the relative proportions of the component ferrites present in the composite. The maximum of curve 16 of FIG. 2 may be moved to regions of lower frequency, if desired, by an increase in the relative amounts of the ferrites whose losses are shown as curves 11 and 12, for example, if such is desirable for a given use of the composite. Conversely, a shift to higher frequencies may be accomplished by the inclusion of increased proportions of the ferrites represented in curves 14 and 15.

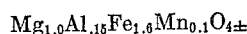
The curves 11 through 15 represent measurements on the following ferrite compositions, in order:



By the choice of a combination of magnetic oxides different from that illustrated in FIG. 1, a suitable composite may be obtained which shows resonance absorption in another portion of the frequency spectrum altogether.

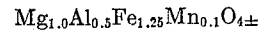
The loss ratios measured in FIG. 1 were for a unidirectional wave directed along the longitudinal axis of a helix of the ferrite being tested. A direct-current magnetic field directed axially along the helix gave a longitudinal field of between about 300 gauss and 600 gauss. A circumferential component of the field around the helix of the ferrite was responsible for interaction with the wave.

The effect of changes in the proportion or composition of the individual compositions making up the final inhomogeneous structure is shown in FIG. 2. Curve 16 of that figure represents the loss ratio dependence on frequency of the composite shown also in FIG. 1. Curve 21 of FIG. 2 shows the shift in maximum absorption to a frequency approximately 0.8 kilomegacycle lower occasioned by a slight variation in the composition giving curve 16. The ferrite

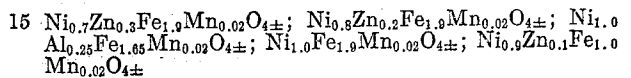


represented by curve 15 of FIG. 1 has been changed from 20 percent by weight of the material of curve 16 to only

10 percent by weight of the material of curve 21, while 10 percent by weight of the ferrite



showing a maximum absorption of 16 decibels at 1 kilomegacycle, has been substituted. Curve 22 shows the characteristics of a composite different entirely in composition from the structures in curves 16 and 21. The choice of ferrites has been such that maximum absorption occurs at a frequency of about 6.6 kilomegacycles, with absorption extending to lower than 2 kilomegacycles. Curve 22 shows the absorption characteristics of a composite of the following five ferrites, taken in equal proportions by weight:



The measurements presented graphically in FIG. 2 were made under the same conditions as those described for the samples of FIG. 1.

In FIG. 3, the empirically determined absorption characteristics of the composite represented by curve 16 in FIGS. 1 and 2 are compared with curve 31, the weighted mathematical summation of curves 11 through 15 of FIG. 1. The curves show the measured absorption characteristics of the composite and the calculated absorption values which would be obtained if an equal quantity of effective absorbing material were to be assembled, for example in tandem, from the five separate ferrites making up the composite. Under the experimental conditions, described for FIG. 1, used in measuring the absorption indicated by curve 16, the length of the ferrite helix tested was critical in determining the amount of absorption of the helix at a given frequency. The curve 31 would then, for example, represent the absorption of a helix of equal length as that measured for curve 16, but composed of five joined pieces, each one-fifth of the total length, of the separate ferrites used in manufacturing the composite measured in curve 16.

The good match of the calculated curve 31 with the empirical curve 16 shows that the absorption of a proposed composite may be predicted with fair accuracy from a curve summing the loss curves of the component materials proposed for the composite structure.

FIG. 4 is a representation in section of the structure of a composite ferrite produced by the methods of the present invention magnified by a factor of about 50. In FIG. 4 the inhomogeneity of the structure depicted is visually apparent. Some portions of the structure, for instance areas 41 and 42, appear to have fairly clearly defined boundaries. Other distinguishably dissimilar portions, for example 43 and 44, different in appearance and also probably different in composition, merge almost indistinguishably in a zone created by diffusion during sintering. Very clearly bounded areas 45 are, apparently, voids in the fired structure. Portions 41, 42, 43 and 44 have no reference to specific ferrite compositions, and are representative of different portions of any of the fired inhomogeneous compositions mentioned hereinafter.

Inhomogeneous structures of the kind here considered may be formed from any combination of ferrites. Depending on the broadband characteristics sought, the nature, number, and proportions of the component materials can be varied. The relatively good correlation between the empirically measured curve of a composite and the weighted mathematical summation of the absorptions observed for the individual ferrites, as shown in FIG. 3 for example, permits a good estimation of the absorption characteristics of a proposed composite before experimental testing of the compounded and fired product.

Among the ferrites that have proved useful in the manufacture of the broadband composites are the following. In the formulas, uncertainty concerning the amount of oxygen bound with the metallic constituents is reflected by the plus-minus notation on oxygen content. This un-

certainty arises from a lack of exact knowledge of the extent of oxidation or reduction of the metallic materials, particularly iron, after firing.

- (1) $Mg_{1.0}Al_{0.5}Fe_{1.25}Mn_{0.1}O_{4\pm}$
- (2) $Mg_{1.0}Al_{0.35}Fe_{1.4}Mn_{0.1}O_{4\pm}$
- (3) $Mg_{1.0}Al_{0.15}Fe_{1.6}Mn_{0.1}O_{4\pm}$
- (4) $Mg_{1.0}Fe_{1.4}Mn_{0.1}O_{4\pm}$
- (5) $Mg_{0.9}Zn_{0.1}Fe_{1.3}Mn_{0.1}O_{4\pm}$
- (6) $Ni_{0.3}Zn_{0.7}Fe_{1.8}Mn_{0.02}O_{4\pm}$
- (7) $Ni_{0.55}Zn_{0.45}Fe_{1.9}Mn_{0.2}O_{4\pm}$
- (8) $Ni_{0.7}Zn_{0.3}Fe_{1.9}Mn_{0.02}O_{4\pm}$
- (9) $Ni_{0.8}Zn_{0.2}Fe_{1.8}Mn_{0.02}Co_{0.075}O_{4\pm}$
- (10) $Ni_{0.8}Zn_{0.2}Fe_{1.8}Mn_{0.02}O_{4\pm}$
- (11) $Ni_{0.8}Zn_{0.2}Fe_{1.8}Mn_{0.02}O_{4\pm}$
- (12) $Ni_{1.0}Al_{0.25}Fe_{1.65}Mn_{0.02}O_{4\pm}$
- (13) $Ni_{1.6}Fe_{1.9}Mn_{0.02}O_{4\pm}$
- (14) $Ni_{0.9}Zn_{0.1}Fe_{1.9}Mn_{0.02}O_{4\pm}$

The list of ferrite materials presented is exemplary only, and is not to be construed as limiting combinations possible in composites formed by the method described herein. As mentioned, any ferrites may be combined if the properties of the composite produced are desirable. The known ferrites containing magnesium, copper, manganese, cobalt, and nickel, alone or in combination, as well as other lesser known ferrites are adaptable to combination by the method of the invention.

For compounding the composite ferrite structures described above, the individual ferrite components are first separately prepared by techniques known in the art. These techniques comprise sintering reactive compounds of the metals whose oxides make up the ferrite. These starting compounds may be oxides or compounds convertible to oxides, such as hydroxides or carbonates.

Sintering converts compounds to oxides, if other than oxides are used as a starting material, and reacts the oxides to form the ferrite. The sintered material may be ground and resintered one or more additional times to insure uniformity in the final ferrite composition. After the last sintering step in the preparation of each of the constituents desired to be formed into a composite, the fired composition is ground, conveniently by the usual ball-milling techniques.

The milling may be done dry, but is conveniently carried out in the presence of water, acetone, alcohol, or carbon tetrachloride. A binder and lubricant may be added during the milling, polyvinyl alcohol or "opal wax" (hydrogenated castor oil) being preferred when ball-milling with water. Paraffin or "Halowax" (chlorinated naphthalene) are useful with non-aqueous solvents such as carbon tetrachloride.

Each of the ground ferrite materials is then dried by filtration and evaporation, for example, and the dried material is screened so that aggregates predominantly ranging in particle size between about 0.5 centimeter and about 0.01 centimeter in the largest dimension are obtained. Particles between about 0.25 centimeter and about 0.01 centimeter in size are also conveniently used. During pressing and firing, a compression and shrinkage of the aggregates to about one-third of their original volume is experienced. Thus, to obtain discontinuities between 0.003 centimeter and 0.2 centimeter in a fired composite, the aggregates before mixing are preferably roughly between about 0.01 centimeter and about 0.5 centimeter in size, as mentioned. Crumbling the aggregates to sizes roughly between 0.25 centimeter and 0.01 centimeter will give discontinuities in the fired body between about 0.1 centimeter and 0.003 centimeter in size. A similar rough correspondence in the aggregate size to be employed and the size of the discontinuities wanted in the fired body can be worked out in other cases. After screening as mentioned above, the individual ferrite aggregates are combined, one with another, in the proportions desired in the final composite.

This combination is critical. Mixing of the individual materials should not be so thorough that diffusion, pos-

sibly induced by the final firing of the pressed composite, would bring about homogenization of the body. Mixing should be sufficient to bring about a distribution of each of the individual ferrite components throughout the final mixture; yet, in any portion of the body, discrete localities of the individual materials should be maintained.

This mixing may be done by tumbling the component ferrites together by hand for a short time, not usually exceeding a minute or two. Tumbling can also be done by standard tumbling equipment, usually for even shorter periods of time than for hand mixing, perhaps, for example, for a 30 second interval. Mixing, in any case, should not be carried out for such time as will pulverize any substantial portion of the ferrite aggregates to sizes below 0.01 centimeter, as set forth above.

When aggregates of comparatively large size are being mixed, mixing can be more thorough than when smaller particles are mixed. For the larger particles, the size of the particle itself assures some inhomogeneity to a given section of material, even if some diffusion occurs on firing. If small particles are too thoroughly mixed, firing, especially for long periods may cause homogenization of the structure through diffusion, with a resultant loss of the presence of the individual distinct components. The use of aggregates much below 0.01 centimeter usually affords too great opportunity for homogenization during firing, especially where mixing has been too thorough or firing too long, to make aggregates smaller than 0.01 centimeter in size of much interest.

After mixing, the material may be formed by pressing. Forming is facilitated by a binder optionally included in the component aggregates, as discussed. Forming may be done without a binder present also, with perhaps a small amount of moisture being either retained in the aggregates before mixing or being added to the mixed materials before pressing. Forming is usually done at pressures between 10,000 pounds per square inch and 50,000 pounds per square inch.

If a binder has been incorporated into the pressed detail, the detail is conveniently dewaxed after pressing by heating in air. A convenient schedule for dewaxing comprises bringing the pressed parts to a temperature of 400° C. over a 6 hour period and then maintaining a 400° C. temperature over another 6 hour interval.

It is to be noted that the function of the binders or lubricants previously mentioned herein is to facilitate the pressing operation by giving some coherence of the mixed particles one to another. The lubricant acts also to ease the flow of the solid material under compression in the die during forming. Both binders and lubricants are optionally included, and are not relied upon in the invention in any way to give a preferred arrangement of particles prior to pressing. No preformed layers, or any other ordered arrangement, is maintained by the use of the binders and lubricants. A random mixing is the prime requirement of the invention, so that a product, homogeneous to microwaves, is obtained.

Final firing is carried out at temperatures and for times sufficient to sinter the pressed composites, but not long enough that diffusion sufficient to homogenize the body can occur. Temperatures between 1000° C. and 1400° C. are usual, with a temperature of 1250° C. being best for most firings.

The time for which the ceramic composites are fired varies between 15 minutes and 20 hours, depending on the composition of the composites. If copper-containing components are present, for example, firing times may be short, as copper oxides have a high fluxing activity in the composition. On the other hand, aluminum oxide, for example, is difficult to sinter, and aluminum-bearing ferrites may require heating for periods of time approaching the 20 hour figure. In most other cases, those not involving special treatments, for example, due the copper or aluminum ferrites, a firing time of 3 hours to 5 hours

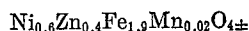
is typical. The composite whose absorption is shown as curve 16 on FIGS. 1, 2 and 3, for example, was fired for 3 hours at 1250° C.

Firing may be done in an atmosphere of air when firing is done at below temperatures of approximately 1200° C. Above that temperature the problems of reduction of the ferrites begin to appear, and firing in an atmosphere higher in oxygen content than that content found in air, or in an atmosphere of pure oxygen, is preferred. These details of firing are known in the art, and may be varied by one skilled in the art practicing the invention to accommodate the method to the ferrite materials with which he is working.

The preparation of a composite ferrite prepared by a preferred manner of practicing the invention is described below. It is to be understood that the example given is illustrative only, and is not to be construed as limiting the scope of the invention in any manner.

Example 1

A ferrite of the composition

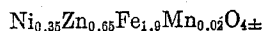


was prepared by mixing the following ingredients in the proportions given:

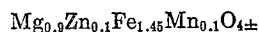
Material:	Parts by weight
NiCO ₃ -----	71.1
ZnO -----	32.6
Fe ₂ O ₃ -----	151.5
MnCO ₃ -----	2.3

Mixing was done for 15 minutes in water in an Eppenbach mill. The mixed material was filtered, dried in an oven at 110° C., and granulated using a 20 mesh Standard screen with sieve openings of 0.84 millimeter. The material was calcined at 900° C. for 16 hours, then ball-milled with water overnight. After milling, the material was again filtered and dried in an oven at 110° C. The dried ferrite was again ball-milled, this time in carbon tetrachloride to which "Halowax" was added in an amount equal to 10 percent by weight of the charge. Milling was continued for about 2 hours, after which the solvent was evaporated from the wax-coated particles while stirring the particles. The resultant conglomerates were then screened on a 60 mesh Standard screen with sieve openings of 0.25 millimeter.

In identical fashion, two ferrites of the compositions noted were separately prepared by mixing the materials listed in the proportions given and subjecting them to further treatment as noted above.

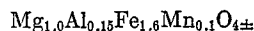


Material:	Parts by weight
NiCO ₃ -----	41.5
ZnO -----	52.9
Fe ₂ O ₃ -----	151.5
MnCO ₃ -----	2.3

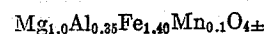


Material:	Parts by weight
MgCO ₃ -----	75.8
ZnO -----	8.1
Fe ₂ O ₃ -----	115.8
MnCO ₃ -----	11.5

Two more ferrites were separately prepared as in the preceding examples, except that calcining was carried out at 1000° C., rather than 900° C. Their compositions are given below, with the ingredients used in compounding them.



Material:	Parts by weight
MgCO ₃ -----	84.3
Al(OH) ₃ -----	11.7
Fe ₂ O ₃ -----	127.6
MnCO ₃ -----	11.5



Material:	Parts by weight
MgCO ₃ -----	84.3
Al(OH) ₃ -----	27.3
Fe ₂ O ₃ -----	111.7
MnCO ₃ -----	11.5

After preparation of the five ferrites as outlined above, equal portions by weight of each of the dry powdered aggregates were loosely mixed by hand for about a minute. The mixed aggregates were placed in a die block and compressed under a pressure of about 20,000 pounds per square inch. The pressed composite was dewaxed by heating the material from room temperature up to 400° C. over a period of six hours, and maintaining the composite at that temperature for another 6 hour period.

The composite was then fired at 1250° C. for 10 hours in an atmosphere of oxygen.

The broadband resonance properties of the fired composite are shown as curve 16 of FIG. 1.

What is claimed is

The method of preparing a composite ferrite body showing broad-band resonance absorption for microwaves which comprises separately sintering five ferrite compositions which individually show resonance peaks at spaced intervals within the frequency spectrum for which broad-band resonance is desired, the metallic constituents of said compositions being present in the following amounts, the non-metallic constituent being oxygen:

30	Mg _{1.0} Al _{0.35} Fe _{1.4} Mn _{0.1}
	Mg _{1.0} Al _{0.15} Fe _{1.6} Mn _{0.1}
	Mg _{0.9} Zn _{0.1} Fe _{1.3} Mn _{0.1}
	Ni _{0.35} Zn _{0.65} Fe _{1.9} Mn _{0.2}
35	Ni _{0.6} Zn _{0.4} Fe _{1.9} Mn _{0.02}

powdering said sintered ferrite compositions, screening said powdered ferrite compositions to obtain ferrite aggregates between 0.01 centimeter and 0.5 centimeter in their longest dimension, loosely mixing in approximately equal parts by weight said different ferrite aggregates but retaining in said mixture aggregates 0.01 centimeter to 0.5 centimeter in their longest dimension, shaping a body from the mixture so prepared and firing said shaped body in an oxidizing atmosphere at a temperature between 1000° C. and 1400° C. for a time sufficient to sinter said mixture without extensive homogenization of said mixture by interdiffusion between said different ferrite regions, whereby a composite structure, homogeneous in gross but rendered inhomogeneous by the presence of a mixture of discrete regions composed essentially of the individual component ferrites is produced, said regions being between about 0.003 centimeter and 0.5 centimeter in their largest dimension.

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