

July 25, 1961

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2,994,045

ELECTRICAL TRANSMISSION DEVICES UTILIZING GYROMAGNETIC FERRITES

Filed April 11, 1955

3 Sheets-Sheet 1

FIG. 1

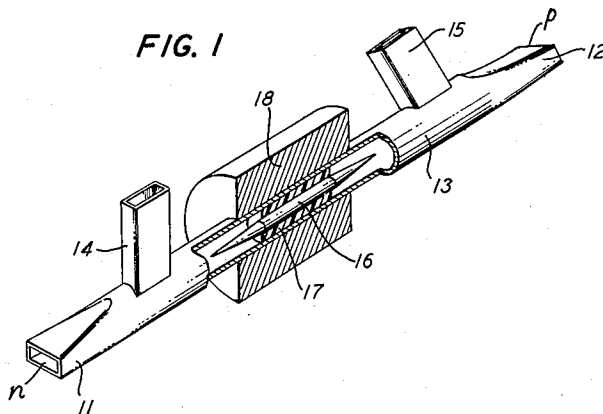


FIG. 2

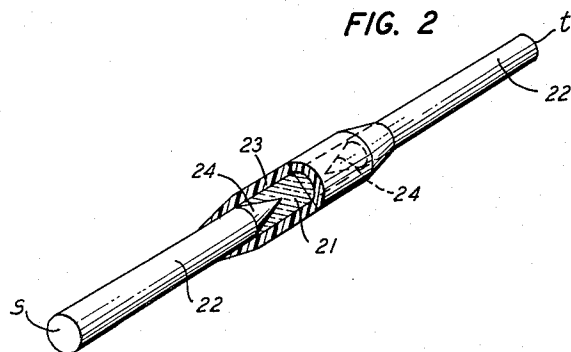


FIG. 4

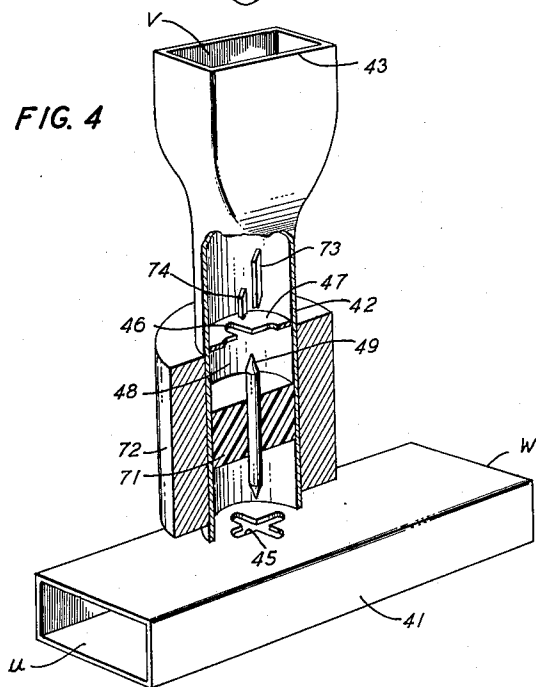
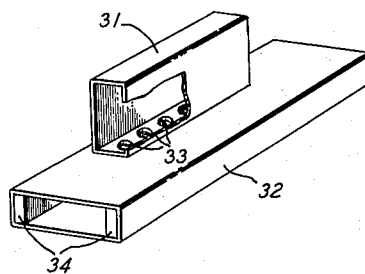


FIG. 3



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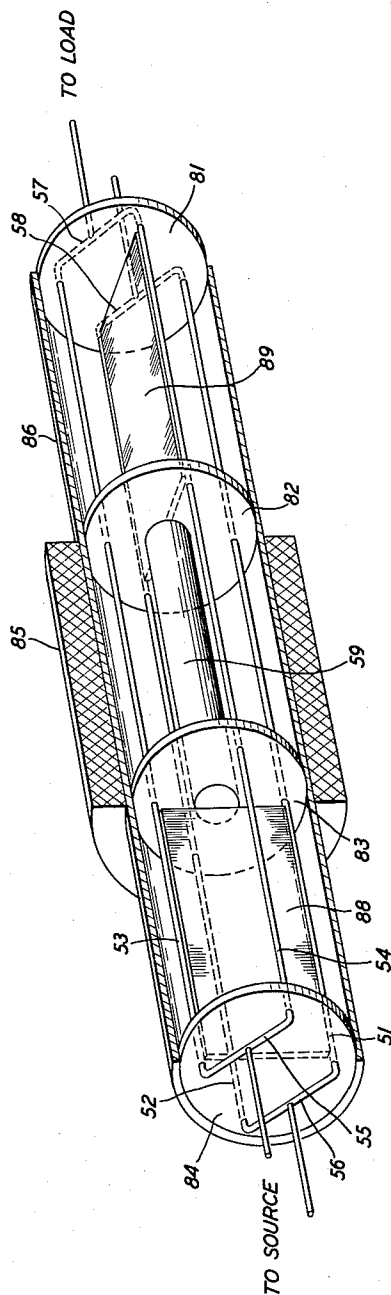
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FIG. 5



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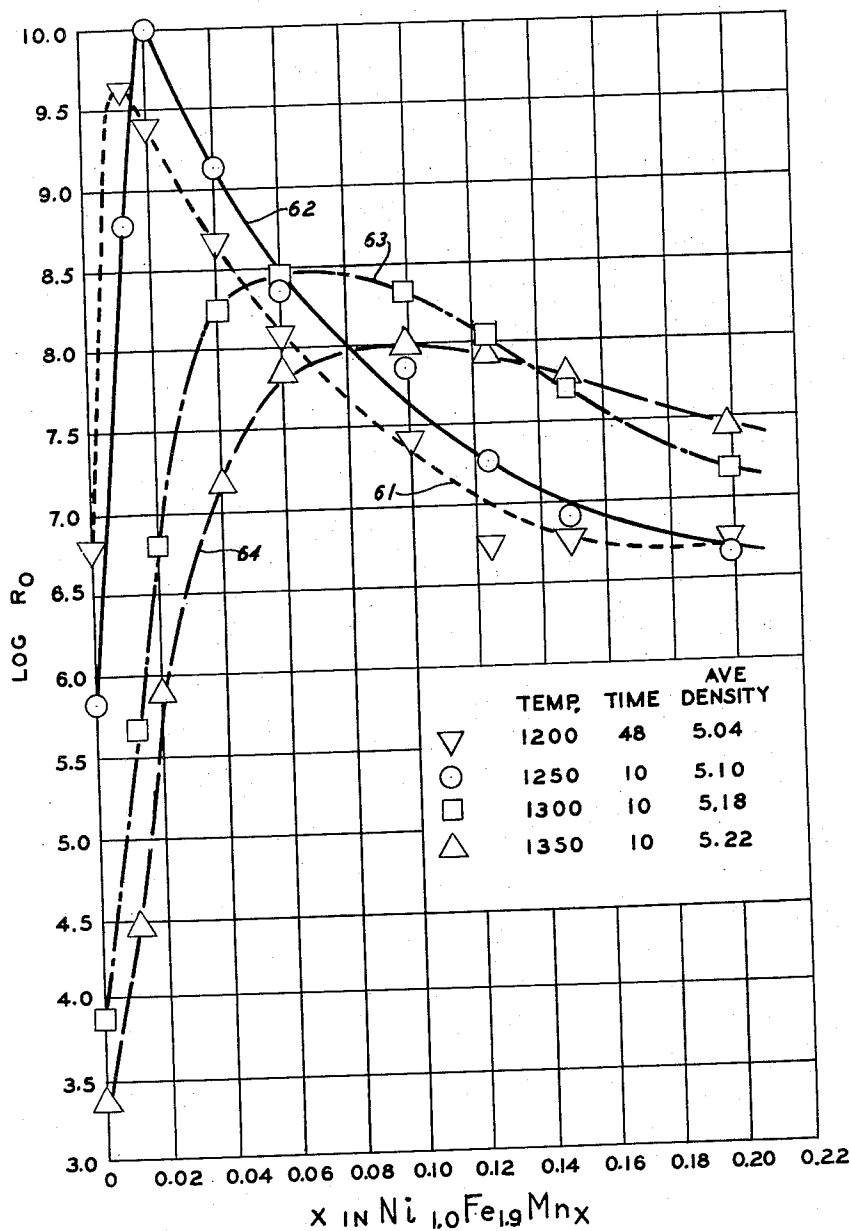
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ELECTRICAL TRANSMISSION DEVICES UTILIZING GYROMAGNETIC FERRITES

Filed April 11, 1955

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FIG. 6



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ELECTRICAL TRANSMISSION DEVICES UTILIZING GYROMAGNETIC FERRITES

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Filed Apr. 11, 1955, Ser. No. 500,451
5 Claims. (Cl. 333-24)

This invention relates to ferrite materials, and to devices for the transmission of high frequency electrical signals, said devices being constructed in part of ferrite materials, and utilizing the gyromagnetic properties of said ferrite materials. Particularly, it relates to such devices for which said gyromagnetic ferrite materials are high-resistivity compositions deficient in iron and comprising small quantities of either manganese or cobalt, or both, and to said ferrite materials themselves.

In the construction of the above-mentioned devices, different modifications of which may be used to transmit waves having frequencies between 300 megacycles per second and 50,000 megacycles per second, it is desirable to use ferrite bodies which reduce indiscriminate attenuation of the signal through loss to a minimum. One factor influencing such losses is the resistivity of the ferrite, and high-resistivity materials are generally to be preferred. Other properties of the ferrites are equally important in any given application, however, and it is often difficult to find ferrite compositions which are otherwise suitable which have, also, resistivities which are as high as may be desired.

It has been found that the addition of small amounts of manganese or cobalt, or both, to ferrite compositions may increase their direct-current resistivities to values which permit the effective use of the resulting ferrites in a variety of applications, particularly those utilizing frequencies within the range mentioned above.

The figures in the accompanying drawings are intended to be exemplary of some types of devices for which the gyromagnetic ferrites disclosed herein have been found particularly useful. The operation of these and similar devices, and the principles governing the use of the gyromagnetic properties of ferrite materials in devices for electrical transmission systems, particularly microwave systems, are fully discussed in the paper "Behavior and Applications of Ferrites in the Microwave Region," by A. G. Fox, S. E. Miller, and M. T. Weiss, published in the Bell System Technical Journal, volume 34, No. 1, January 1955, pages 5 through 103.

In the accompanying drawings:

FIG. 1 is a perspective view, partly in section, of a Faraday-rotation type of circulator mounted in a hollow metallic waveguide;

FIG. 2 is a perspective view, partly in section, of a round dielectric waveguide containing a ferrite loading for producing Faraday-rotation;

FIG. 3 is a perspective view, partly in section, of a directional coupling device utilizing non-reciprocal field displacement;

FIG. 4 is a perspective view, partly in section, of a device having a ferrite-loaded resonance cavity;

FIG. 5 is a perspective view, partly in section, of a ferrite-loaded non-reciprocal attenuating device employing a balanced wire line transmission system; and

FIG. 6 is a chart showing, for several firing temperatures, the dependence of the resistivity of some of the ferrite compositions herein disclosed on their manganese content.

In FIG. 1, rectangular waveguides 11 and 12 are tapered smoothly into a circular waveguide 13. The rectangular

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waveguides 14 and 15 are joined to the circular waveguide 13 near a rectangular guide 11 at the left-hand end, and near a rectangular guide 12 at the right hand-end, respectively. If imaginary planes be passed through each of the four rectangular waveguides 11, 12, 14, and 15, parallel to the longest dimension of the rectangular section, the positioning of the guides 11 and 14 will be such that the planes mentioned above for this pair of guides will intersect perpendicularly. Similarly, the guides 12 and 15 are set at right angles to one another at the right-hand end *p* of the drawing shown. The planes passing through the guides 11 and 12, are, further, inclined to one another at an angle of 45 degrees, and the waveguides 14 and 15 are similarly relatively inclined at an angle of 45 degrees.

In sum, there are two pairs of guides, 11 and 14, and 12 and 15, the members within a pair being disposed at right angles. Both members of one pair, say waveguide 12 and waveguide 15, are rotated 45 degrees with respect to the members of the first pair, however, so that for any member of either of the two pairs of perpendicular waveguides there is a corresponding member of the other perpendicular pair inclined to the first member at an angle of 45 degrees.

Within the circular waveguide 13 is a pencil 16 of the ferrite materials considered later herein, mounted in a non-magnetic dielectric material 17, such as, for example, polystyrene foam. Surrounding the ferrite pencil 16 is a magnetic source 18, such as an electromagnet or permanent magnet, capable of producing a longitudinal magnetic field.

In a magnetic field, a ferrite element has the property of rotating the plane of polarization of an incident plane polarized wave. The rotation produced in the element 16 shown, for example, is determined by the nature of the ferrite used, by the dimensions of the ferrite element 16, and, in addition, by the strength of the magnetizing field from the field source 18, and by the specific geometry of the waveguide 13 and the mounting of the element 16 therein. The sense of the Faraday-rotation is determined by the direction of the magnetizing field.

In the circulator shown in FIG. 1, for example, the length of the element 16 and the strength and direction of the magnetizing field from the source 18 may be chosen to give a 45-degree counterclockwise rotation viewed from *n* to *p*, in FIG. 1, for waves passing through the element 16 from *n* to *p*. In passing from *p* to *n*, waves are rotated in the same sense by the ferrite.

Thus, waves electrically polarized perpendicular to the longest dimension of the rectangular section of the waveguide 11 pass the guide 14 and penetrate the ferrite 16. As the geometry of the guide 14 is such as to transmit only waves polarized perpendicularly to those entering at 11, the waves entering 11 are unaffected by passing the guide 14. In the ferrite, a 45-degree counterclockwise rotation results, and the wave plane is oriented for transmission out through guide 12. Again, the outgoing wave is unaffected by the guide 15 set at right angles to the plane of the polarized wave in guide 12. If a wave enters the guide 12, reversing the direction of transmission in the original illustration, it passes guide 15, is rotated by the ferrite in the same sense as before, and is thus, this time, oriented for transmission through the guide 14. By similar considerations, waves entering guide 14 are made to exit through the guide 15; and waves entering the guide 15 leave, after rotation, by waveguide 11.

A more detailed explanation of the device described above is to be found in the copending application of S. E. Miller, Serial No. 263,600, filed December 27, 1951, now U.S. Patent No. 2,748,352.

FIG. 2 shows a Faraday-rotation device comprising a

ferrite loading 21 in a round dielectric waveguide 22. The ferrite 21 comprises the materials considered later herein, and the waveguide 22 may consist of any dielectric material having a dielectric constant materially different from that of air, such as, specifically, polystyrene or polyethylene.

Electromagnetic waves are transmitted through dielectric media similar to that used in the construction of the waveguide 22 without a conductive shield surrounding the transmitting medium. The wave is guided by the dielectric, with a portion of the energy conducted in a field surrounding the rod. By joining the dielectric rod 22 with the ferrite segment 21, a portion of the wave energy can be led through the ferromagnetic material and can be thereby affected. As in FIG. 1, permanent magnets or electromagnets, not shown, are used to produce a horizontal magnetic field in the region of the ferrite and rotation of the wave traversing the ferrite is effected. Tapered portions 24 of the dielectric rod 22 fit into conical hollows in the ferrite rod 21 to assure matching and to minimize possible radiation loss. An additional cylindrical cover 23 of dielectric material is provided over the ferrite segment to aid in maintaining a constant energy field which might otherwise be disrupted by disparity between the indices of refraction of the ferrite material 21 and the dielectric 22.

In operation, a linearly polarized wave, for example, introduced at *s* into the waveguide 22 is propagated through the ferrite 21 and emerges at *t* with a rotation in the angle of polarization. Means, not shown, may be provided for utilizing the rotation observed in the construction of a circulator, as in FIG. 1, or the segment of the circuit shown in FIG. 2 may be adapted to other purposes.

A complete and detailed explanation of devices employing ferrite-loaded dielectric waveguides is to be found in the copending application of A. G. Fox, Serial No. 304,609, filed August 15, 1952, now U.S. Patent No. 2,787,765.

FIG. 3 shows a multibranch network in which gyro-magnetic materials are used to create field displacement effects. Shown are two rectangular metal waveguides 31 and 32. The guide 31 is placed with one narrow wall contiguous to a wide wall of the guide 32, and is so located as to lie off the center line of said guide 32. Apertures 33, extending through the contiguous walls of the guides 31 and 32, are used to couple the guides 31 and 32 electromagnetically. These apertures, lying on the center line of the narrow wall of the guide 31 are displaced, as is the guide 31 itself, from the center line of the guide 32.

Within the guide 32, and in the region of the coupling apertures 33, are means for producing a non-reciprocal displacement of the magnetic field pattern therein, comprising, in this case, two slabs 34 of a ferrite material as later described herein. Means, not shown, such as a solenoid or permanent magnet, are provided for creating a uniform magnetic field in each of the ferrite slabs 34, so that said slabs are magnetically polarized at right angles to the direction of propagation of wave energy in the waveguide 32. Both slabs 34 are polarized in the same direction.

In a rectangular waveguide such as that shown in FIG. 3 as 32, the magnetic field of a dominant mode wave being propagated through the waveguide will be such that a clockwise-rotating and a counterclockwise-rotating component of the magnetic intensity will be found respectively at one or the other extremity of the longest rectangular dimension of the waveguide wall. That is, depending on the direction of wave propagation, the direction of the polarization at one of the waveguide walls will be clockwise or counterclockwise, with rotation in the opposite sense being found in the magnetic intensity at the other wall for a given direction of wave propagation. Upon reversing the direction of propagation, the sense of the polarization at each wall also reverses.

By biasing the ferrite loadings 34 in a magnetic field

perpendicular to the length of the waveguide 32, as previously mentioned, each element being polarized in the same direction, the electron spins and associated moments within the ferrite can be caused to precess about the line of the biasing magnetic field on the ferrite, producing a magnetic moment rotating in a plane normal to the biasing field, or, that is, in the plane of the magnetic component of the waves propagated along the waveguide 32. The rotating moment produced by electron spin in the ferrite will correspond, on one side of the waveguide or the other, to the rotating component of the magnetic intensity of the wave, resulting in a permeability less than unity for one of the ferrite strips 34. On the other side of the waveguide 32, the biasing field produces precession with a moment in a sense opposite to the rotating component of the wave's magnetic field, resulting in a permeability greater than unity for this second ferrite strip.

The discrepancy in permeability for the two strips 34 results in a displacement of the normal field pattern.

Without the biasing magnetic field applied to the ferrite slabs 34, the magnetic field intensity of the propagated wave in the waveguide 32 is null along the center line of the waveguide, rising to a maximum at the sides of the guide. When a biasing field is applied to the ferrite, the field pattern of the wave may be distorted to give a null value in the region immediately beneath the off-center coupling apertures 33. No coupling results in this case. Reversing the direction of wave propagation in the waveguide 32, without changing the direction of the bias on the ferrite elements 34, will result in a displacement of the null field area to a point on the other side of the center line of the waveguide 32, away from the coupling apertures 33. Coupling of the guides 31 and 32 will result for this direction of wave propagation.

Thus, for one direction of propagation through the waveguide 32, coupling with the guide 31 results, while reversing the propagation direction will produce no coupling with the guide 31.

A more detailed explanation of the device discussed above, and other field-displacement devices, is to be found in the copending application of S. E. Miller, Serial No. 371,437, filed July 31, 1953, now U.S. Patent No. 2,849,683.

FIG. 4 is a perspective view, partly in section, of waveguide structures coupled by a chamber containing a gyro-magnetic ferrite element to produce a three-branch circulator.

In the drawing a hollow rectangular waveguide 41 is abutted by a second waveguide 42 of a type capable of supporting circularly polarized waves. The guide 42 is tapered smoothly into a rectangular waveguide 43 which will transmit linearly polarized waves only. Means, such as positioned metal fins 73 and 74, are so disposed at the junction of waveguides 42 and 43 as to interconvert circularly polarized waves in guide 42 to and from linearly polarized waves in guide 43, by introducing a 90-degree phase shift in selected components of the impinging waves.

A resonant cavity 48 is formed in the lower portion of the waveguide 42, said cavity being bounded at the top by a perforated reactive diaphragm 47 and at the bottom by the waveguide 41. The diaphragm 47 is so positioned as to render the length of the cavity 48 a multiple of one-half of the guide wavelength of the waves to be transmitted therethrough. Apertures 45 and 46 couple wave energy to and from guides 41 and 42 and guides 42 and 43, respectively.

The aperture 45 is of such geometry and is so positioned, by techniques known to those skilled in the art, relative to the waveguides 42 and 41, that for waves transmitted through waveguide 41 from *u* to *w* in the diagram, a circularly polarized wave will be introduced into the cavity 48, while for those waves transmitted through the guide 41 from *w* to *u*, a wave circularly polarized in the opposite sense will be found in the cavity 48.

Within said cavity 48 is mounted an element 49 of a gyromagnetic ferrite of the kind later considered herein. The ferrite 49 is mounted in a material 71 of low dielectric constant, such as "polyfoam." Surrounding the cavity 48 in which the ferrite 49 is located are means 72, such as a solenoidal winding, for producing a steady polarizing magnetic field parallel to the direction of wave propagation in the waveguide 42.

In a gyromagnetic ferrite similar to that of the element 49 in the drawing, polarized by a biasing magnetic field, the permeability presented to circularly polarized waves transmitted therethrough is different for waves polarized in opposite senses, as earlier mentioned. When the sense of the wave polarization is coincident with the sense of the rotating magnetic moment associated with the precession of electron spins in the ferrite, the permeability of the ferrite has a value above unity. When the senses of the wave and the moment in the ferrite are opposite, the permeability of the ferrite is less than unity for biasing fields insufficient to produce resonance in the ferrite. Depending on the strength of the field, further, the ferrite permeability may take values less than zero.

The circulator shown in FIG. 4 employs this gyromagnetic property of the ferrite element 49 in its operation. For illustration, let the position of the aperture 45 be such as to produce a counterclockwise polarized wave in waveguide 42 when a wave is transmitted along guide 41 from *u* to *w*. Further, let the biasing field from the source 72 be in a direction as to permit transmission of such a polarized wave through the ferrite element 49 in the cavity 48. When the cavity 48 is made of a length which is a multiple of the half wavelength of the transmitted wave, by positioning of the diaphragm 47, the cavity 48 is resonant for the wave, and the wave, after conversion by the fins 73 and 74 appears as a linearly polarized wave at *v*.

A wave transmitted in waveguide 41 from *w* to *u*, however, will be clockwise polarized in waveguide 42, in this example. The biasing field on the ferrite 49 produces a low permeability for such a wave, and no resonance or transmission to terminal *v* ensues. Waves introduced at *w*, thus, emanate only at *u*.

The introduction of wave energy at *v* results, for the position of the fins 73 and 74 chosen, in the introduction of a counterclockwise rotation. Such a wave, as seen earlier, will be resonant in the cavity 48, and will be coupled into the waveguide 41. Passage through the aperture 45 by such a counterclockwise polarized wave will result in a wave, the magnetic components of which are characteristic of waves being transmitted from *u* to *w* in the example under discussion, and emergence of the wave at *w* will result. By adjustment of the size of the apertures 45 and 46, the impedances of the terminals *u*, *v*, and *w*, which terminals are coupled by the apertures through the cavity 48, can be matched as to give transmission without reflection along the paths *u* to *v*, *v* to *w*, and *w* to *u*, so that the element pictured is a non-reciprocal circulator.

Though the ferrite elements previously shown have been incorporated in devices particularly useful in the microwave region, they may be also used in the construction of devices to be used in the ultra-high-frequency and very-high-frequency range, below a few thousand megacycles.

In FIG. 5 is shown one such circuit element, which may be used as an isolator, suitable for connection directly into a two-wire balanced line transmission system. The embodiment pictured comprises two pairs of parallel conductors 51, 52, 53 and 54, equally spaced and symmetrically aligned relative to each other. The conductors are bridged in pairs by connecting elements 55, 56, 57 and 58.

Thin discoid dielectric spacers 81 through 84 are longitudinally placed along the line to support the conductors in their above-described relationship. Spacers 82 and 83, in addition, may serve to support a gyromagnetic ferrite

body 59 comprising materials of the type herein later described. A shield 86 serves to support the structure and protects the conductors 51 through 54 from external mechanical and electrical influences. A longitudinal magnetic field is supplied by a winding 85 to polarize the ferrite 59. Control of the energizing field is provided so that strengths sufficient to produce a ferromagnetic resonance condition in the ferrite 59 may be produced if desired.

Loading vanes 88 and 89 are disposed, respectively, between the wire pairs 51 and 53 at the right-hand end of the circuit element shown, and between the pairs 52 and 54 at the left-hand end. The vanes, of a material having a high dielectric constant, extend longitudinally between the wire pairs mentioned for a length sufficient to introduce a 90-degree delay in a voltage between the conductors comprising a pair.

When a voltage, balanced with respect to ground, is applied between the bridges 55 and 56, the voltage between conductors 54 and 53 is delayed by 90 degrees by the vane 88. Similarly, a 90-degree shift in voltage between the lines 52 and 51 is produced by the dielectric material 88. In consequence, a circularly polarized wave is produced by the four-wire system in the region of the ferrite loading 59. Upon passing the loading 59, the vane 89 reintroduces 90-degree voltage delays in the conductors, in a fashion similar to the operation of the vane 88, so that a balanced voltage is again applied to the load on the far side of the ferrite body 59.

If the rotation produced in the polarized wave in the region of the ferrite 59 is similar in sense to the precession of electron spins and the moment associated therewith in the ferrite, the wave is transmitted almost unaffected by the conductors 51 through 54 from the source to the circuit load. If the polarized wave rotates in a sense opposite to the rotating magnetic component generated in the ferrite 59, however, almost no transmission past the ferrite is observed when the ferrite is excited to its resonant frequency by the magnetic source 85. Since attempted transmission in opposite directions through a circuit element such as that shown in FIG. 5 will produce waves polarized in opposite senses in the supporting conductors 51 through 54, the element shown may be used as an isolator, permitting transmission in one direction only, when the ferrite biasing field is maintained in a constant direction and at a strength producing a ferromagnetic resonance condition in the ferrite material 59.

A more complete and detailed description of the balanced wire transmission system described above, and others, is to be found in the copending application of A. M. Clogston, Serial No. 485,281, filed January 31, 1955, now U.S. Patent No. 2,892,161.

In each of the above-described devices, as well as in other transmission devices wherein the operation of the device is dependent upon the gyromagnetic properties of the ferrite, it is desirable, as stated above, that indiscriminate losses in the ferrite be maintained as low as possible by providing a ferrite which has the highest possible resistivity as well as the other requisite characteristics. FIG. 6 depicts graphically one aspect of the resistivity behavior of a ferrite typical of those described herein.

In the chart shown in FIG. 6, the ordinate measures the logarithm of the resistivity of several nickel ferrite compositions containing added manganese, with the abscissa indicating the manganese content of these compositions. As noted, curves 61, 62, 63 and 64 respectively depict the dependence of resistivity on manganese content for ferrite compositions fired at 1200° C., 1250° C., 1300° C. and 1350° C.

The introduction of a small amount of manganese into a nickel ferrite composition can be seen to cause an abrupt increase in resistivity in the ferrite. In each case, an optimum manganese content is apparent, resulting in a maximum in the resistivity. This maximum is shifted

to higher manganese concentrations as the firing temperature is increased. At still higher manganese concentrations, all the resistivity curves appear to approach an asymptotic value of about 7.0.

For this specific series of ferrites, the more pronounced peaks in resistivity are seen to appear in the materials fired at the lower temperatures.

Conduction in ferrite materials is generally considered dependent upon the presence of metal ions in more than a single valence state within the ferrite. For example, conduction in a nickel ferrite is probably effectuated by electron transfer between ions of divalent and trivalent nickel, and also between divalent and trivalent iron. Though the ferrite may be compounded with divalent nickel salts or oxides and with ferric salts or oxides, considerable quantities of oxygen may be absorbed by the ferrite upon cooling after firing, presumably as some of the nickelous material is converted to nickelic compounds. Conversely, during firing some reduction of ferric iron to a divalent state may occur, and if cooling is rapid, reconversion of the ferrous iron to the trivalent state may not be completely accomplished. The introduction of any impurities such as ferrous iron or nickelic nickel into a ferrite tends to reduce the resistivity of the pure ferrite. However, to control the manufacturing process to yield only a pure material, free of such contaminants, is prohibitively impractical. The requirement of preventing over-oxidation of nickel, for example, while simultaneously preventing the reduction of ferric iron in a pure ferrite, is one which does not admit of an easy practical solution by a manipulative technique alone.

The addition of cobalt or manganese compounds, or mixtures thereof, to an iron-deficient ferrite appears, however, to suppress the easy conductivity mechanisms associated with the $Ni^{2+}-Ni^{3+}$ and $Fe^{2+}-Fe^{3+}$ couples, replacing them with conduction paths much less efficient. Though the resultant materials may be of lower resistivity than that expected to be shown by an absolutely uncontaminated ferrite, such cobalt and manganese addition results in a net increase in resistivity for ferrites prepared by usual techniques. The practical effect of such additions is to yield materials of resistivities higher than those observed for ferrites of the same composition, without the added elements, prepared by the same processes.

Cobalt and manganese are themselves contaminants for ferrites. If they were to be added in excessive amounts, such addition might result in lowering the resistivity of the ferrites to values lower than those normally observed when the ferrites are contaminated only by trace quantities of ferrous iron. Consequently, the amount of the added elements is kept small.

Thus, good ferrites are obtained when the atom percent of these added metals is kept between the values 0.167 and 2.67, calculated on the basis of the total number of metal atoms present in the composition. The better ferrites preferably contain no more than 2.00 atom percent of added cobalt, manganese, or their mixture, and, more preferably, contain less than 1.67 atom percent of these ingredients. In the ferrites containing nickel, the best materials are found to contain less than 1.32 atom percent of the added elements.

As a preliminary aid in the suppression of the appearance of any ferrous iron in the compositions, the ferrites are compounded to give an iron-deficient material. Such an iron deficiency greatly reduces the tendency to formation of Fe_3O_4 in solid solution with the ferrite. By inhibiting the formation of such a solid solution of magnetite with the ferrite, the presence of ferrous iron in more than trace amounts is avoided. Such trace amounts can then be eliminated by manganese or cobalt additions.

As used herein, the term "iron deficiency" will sig-

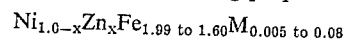
nify a departure from the stoichiometry represented by the generalized ferrite formula



for which, it is seen, two iron atoms are present for each divalent metal atom A. For the "iron deficient" materials herein, the ratio of the number of atoms of iron or of iron and added aluminum, if any, to the total number of divalent atoms of other metals present will fall beneath the value 2.0. The ratio mentioned above preferably will take values intermediate to an upper limit of 1.99 and a lower limit of 1.6, though more deficient compositions are possible if replacement of iron with other trivalent atoms, such as aluminum, is accomplished. In some cases, when aluminum is present, the ratio mentioned may reach a value of 1.5 in the compounding of desirable materials.

Four ferrite systems in which the modifications of cobalt and manganese addition and iron deficiency have proved particularly effective in increasing resistivity can be used to advantage in illustrating the present invention. Though some overlapping of these four categories may occur, as will be apparent in the discussion below, the division presented has been found to have the greatest expository clarity.

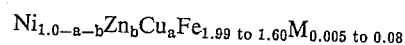
The first such ferrite system to be used for illustration comprises the nickel-zinc ferrites. The compositions contemplated in the present case may be described by reference to the metallic constituents present in the composition only, the non-metallic element required for a charge balance being understood to be oxygen. For the nickel-zinc ferrites under discussion, the component metals are present in the following proportions:



where M may be manganese or cobalt or mixtures thereof. The subscripts signify the relative number of gram atoms of the element indicated which are present, and thus are also proportional to the relative numbers of atoms of each metal present in the ferrite composition.

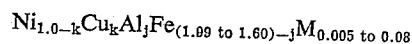
The value of x may lie between 0 and 0.45, and is also usually limited, for the better compositions, to a figure between 0 and 0.40. It can be seen that when x has a null value the ferrites correspond to nickel ferrite with added cobalt or manganese. The content of these latter two materials more preferably may have a value lying between 0.01 and 0.06 in the formula given above, and the most useful compositions are obtained when said content is held between 0.01 and 0.04.

The second ferrite system to be used for illustration may be described as that comprising the nickel-zinc-copper ferrites, with metal contents, as before, indicated by the proportions:



As in the earlier case, M represents cobalt, manganese, or mixtures of these elements. Preferred limits on the content of such additions may be set, as stated, at 0.01 and 0.06, or, more preferably, at 0.01 and 0.04. In the formula given above, b may vary between 0 and 0.45, and a between 0 and 0.40. It can be seen that if a is given a null value, the category includes the nickel-zinc ferrites of the earlier discussion, and if b is also kept at zero, a nickel ferrite is obtained. The zinc content for this second system, b , may also vary between 0 and 0.40 to yield the more useful ferrites in this class, while the copper content, as determined by a , is preferably limited to values between 0.05 and 0.25.

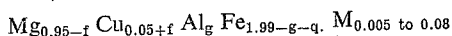
A third specific ferrite system useful for illustration of the principles of the invention comprises nickel-copper-aluminum materials represented generally by the recitation of proportions:



M is again cobalt, manganese, or other mixture.

The subscripts of M are preferably varied to give compositions in which the content of cobalt or manganese lies between 0.01 and 0.06, with the most useful compositions being found when M lies in the range between 0.01 and 0.05. The aluminum content, j , on which is dependent the iron deficiency for this class of materials, may range between 0 and 1.0 in value, though preferred compositions are obtained when the aluminum is kept between the values 0.1 and 0.6. The copper content, k , may lie between 0 and 0.40, though preferred compositions are obtained when the copper content is limited to the range from 0.05 to 0.25.

A fourth ferrite system, the magnesium-copper-aluminum ferrites, contains manganese, cobalt, or mixtures of the two, according to the scheme:



M once more symbolizes the added cobalt, manganese, or cobalt-manganese mixture.

The more useful compositions in this system are obtained when the subscripts on M are limited to values between 0.01 and 0.06, or, more preferably, between 0.01 and 0.05. For this last of the four ferrite systems to be described in detail, the value of f , which is determinative of both the magnesium and the copper content, most generally takes values between 0 and 0.40, though the better ferrites are found when f varies between 0.05 and 0.25. Similarly, the aluminum content, g , which also in part fixes the iron deficiency, is best kept within the overall range 0 to 0.75, though the more useful compositions are obtained when g lies between the values 0.05 and 0.7. Particularly good materials result when g lies between the values 0.05 and 0.25. The parameter q , merely descriptive of the iron deficiencies in these ferrites, may be given a value between 0 and 0.50, or more preferably, between 0.10 and 0.25.

In the preparation of the ferrite compositions described in the categories above, the metallic constituents may be introduced into the preparation as oxides, or as compounds which when fired will yield the oxides. Such other compounds, for example, may be the hydroxides, the oxalates, or carbonates. Particular advantage in the preparation of ferrites containing aluminum is obtained when aluminum hydroxide is the compound from which the ferrite is synthesized. Such advantage stems in part from the greater ease with which aluminum hydroxide is dispersed throughout the ceramic mixture.

Manganese and cobalt are preferably added as the carbonates, though other compounds may, as mentioned, be used.

Further preparation of a ferrite article of a composition disclosed herein is done according to the techniques generally known in the art. A suitable procedure is outlined below, though others may be apparent to those skilled in the art.

The ingredients are first mixed, with or without a preliminary dry mix, in a paste mixer as a slurry. Though an aqueous slurry is generally used, the water solubility of some of the component compounds used may dictate the preferential use of a non-aqueous liquid, as, for example, acetone, carbon tetrachloride, or ethanol. After mixing, the paste or slurry is usually dried by removal of the supernatant liquid by filtration, or, if a volatile liquid has been used, by evaporation.

The dried material may then be calcined in air, oxygen, or other oxidizing medium at a temperature preferably between 800° C. and 1100° C. for from 5 hours to 15 hours. After the calcining, the mixture is broken into particles, for example by ball-milling for a period of 5 hours to 15 hours. A liquid, such as water, ethanol, carbon tetrachloride, or acetone, is preferably used in the ball-mill, as in the paste mixer.

After this grinding, the solid may again be dried by evaporation or filtration, and recalcined according to the calcining procedure set out just above.

A second ball-milling, similar to the first is usually next used again to break up the solid. A binder and lubricant may be incorporated into the ceramic material during this ball-milling step. Polyvinyl alcohol or "Opal Wax" (hydrogenated castor oil) are useful binders when ball-milling with water, and paraffin or "Halowax" (chlorinated naphthalene) are useful when milling with non-aqueous solvents, such as carbon tetrachloride. The binder may be added either as a solid, in which case it is dissolved by the fluid used in the milling, or already in solution in a solvent. For "Halowax," which is most commonly used, an amount of wax equal in weight to 10 percent of the weight of the ceramic solids has been found to give best results. For the other binders mentioned, smaller quantities are usual.

After the completion of the milling step, the solvent may be removed by filtration or by evaporation while the ceramic material and the binder residue are stirred to assure uniform dispersion of the binder throughout the inorganic mixture.

The resultant dried powder, in which the binder is to act as a lubricant during subsequent shaping steps, is preferably then granulated to size. This may be accomplished by forcing the mixture through a sieve, for example, and a No. 20 Standard sieve, with a mesh opening of 0.84 millimeter, has been used for this purpose with success.

A vacuum drying of the granulated particles at a temperature between 40° C. and 50° C. may be optionally introduced at this point if further removal of any possibly remaining solvent is desired.

Forming the granules into the shape desired for use in a particular device next follows, pressures of from 10,000 pounds per square inch to 50,000 pounds per square inch being employed. Generally, the higher pressures are preferred as giving a more homogeneous article. A variety of forms, including slabs and cylinders, is useful in the construction of electrical transmission devices, as may be seen by reference to the drawings.

After shaping, the pressed articles are preferably "dewaxed" by heating in air. A convenient dewaxing schedule comprises bringing the pressed parts to a temperature of 400° C. over a period of 6 hours and then maintaining a 400° C. temperature for an additional 6 hours. This dewaxing step, designed for articles of intermediate size, may be modified by lengthening or shortening the heating period for larger or smaller bodies.

Final firing is generally carried out at temperatures between 1050° C. and 1350° C., depending to some extent on the material fired, and is done in an oxygen-containing atmosphere. For the nickel-zinc ferrites in the first category described earlier, firing at temperatures between 1200° C. and 1300° C. in oxygen has been found best, with optimum results being obtained when the material is fired at 1250° C.

For ferrite compositions containing substantial amounts of copper, particularly the nickel-zinc copper and nickel-copper-aluminum ferrites discussed earlier, the firing temperature may be conveniently reduced to as low as 1050° C., an upper limit still being found at 1300° C. Nickel ferrite containing between 0.05 and 0.25 atom percent of copper, calculated on the basis of the total metal atoms present, may be fired in air in the neighborhood of 1150° C. with excellent high values of density and resistivity in the resultant materials.

For the magnesium-copper-aluminum ferrites, a firing range between 1100° C. and 1350° C. has been found to give good results, with an optimum in the properties of the fired bodies being found at 1250° C. These bodies may be fired in either air or atmospheres containing a greater proportion of oxygen than does air.

It is generally observed that high firing temperatures increase the density of the fired material. As demagnetizing effects introduced by inhomogeneities in a pressed

ferrite composition are generally reduced in high density materials, such high densities are to be desired. High temperature firing, however, increases the possibility that iron may be reduced from the ferric to the ferrous state, with loss of resistivity, so that a compromise must often be reached between high density and high resistivity. The use of copper in the ferrite permits lower firing temperatures to be used, lessening the chance of divalent-iron formation, but may itself lower the resistivity of the resultant material in some other manner. The addition of cobalt and manganese to copper-containing ferrites tends to offset adverse effects of copper addition to ferrites, or tends to augment copper's beneficial effects. The resistivity of the material is preserved or increased while the achievement of high densities at relatively low firing temperatures by copper addition is promoted.

Similarly, when copper is present in the ferrite, the firing time may be kept conveniently at about 10 hours, or, if concentrations of copper near the upper limits given on the concentration values are present, may even be minimized to 3 hours or 4 hours. For those ferrites free of copper, such as the nickel or nickel-zinc ferrites mentioned, firing is preferably carried out for intervals between 10 hours and 20 hours in length.

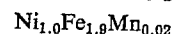
The atmosphere during firing should be, as mentioned, oxygen-containing, and may be of pure oxygen, or air, or a mixture of oxygen with an inert gas such as nitrogen, helium, or argon. The oxygen content is preferably kept at a level equal to, or greater than, that found in air, however. It is desired that the iron content of the ferrites be kept in a fully oxidized condition during firing, and as the dissociation pressure of oxygen over the ferrite materials tends to increase with increasing temperature, pure oxygen or oxygen-rich atmospheres are preferably supplied to the ferrites when firing temperatures near the upper temperature limits previously set are used. When firing nearer the lower-temperature end of the permissible temperature range, the dissociation pressure of oxygen over the ferrites is smaller, and the partial pressure of oxygen in air is sufficiently high to inhibit the reduction of the ferrite compositions by oxygen loss therefrom.

In the following examples are listed several ferrite compositions representative of the four general systems mentioned earlier in illustration of the invention. The examples here are meant to be illustrative only, and are not to be construed as limiting the scope of the invention in any manner.

Example 1

119 grams of nickel carbonate, 152 grams of ferric oxide, and 2.30 grams of manganese carbonate were mixed in an Eppenbach mixer with sufficient distilled water to form a thin slurry. The resultant suspension was dried by filtering and calcined for 15 hours in air at a temperature of 900° C. The calcined solids were then ball-milled for 15 hours in water, filtered dry, and recalcined for a second 15 hour period in air, this time at a temperature of 1000° C. The product of the calcination was again ball-milled in water for 15 hours, filtered, and then dried more thoroughly by heating for several hours in an oven at 110° C. After this oven drying, the product was given a final ball-milling for 3 hours in carbon tetrachloride, during which period sufficient "Hallowax" was added to the slurry to reach 10 percent by weight of the original dry ingredients. The organic solvent was then removed by evaporation while the inorganic component and the wax residue were stirred to promote a homogeneous composition. The mass from which the solvent had been evaporated was granulated by forcing it through a 20 mesh screen, the openings of which are specified by the United States Standard Sieve Scale to be 0.84 millimeter in size. Parts were pressed from the granulated material and dewaxed by heating for 6 hours at 400° C. in air after having been brought to temperature over a six hour period. The pieces were then fired at 1250° C. for 20 hours in pure oxygen.

The resultant material showed a resistivity of 1×10^{10} ohm-centimeters, and had an approximate density of 4.9 grams per cubic centimeter. The metallic components of the ferrite, expressed in gram atoms of the constituents, were present in the following proportions:

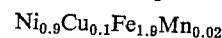


Measurements were made on a tapered rod of the material 2.5 inches in length and 0.160 inch in diameter. The rod was mounted in "polyfoam" in a $\frac{3}{4}$ inch diameter round waveguide section and tested at a frequency of 11.2 kilomegacycles at a magnetic field intensity of 300 oersteds. An insertion loss of 0.04 decibel and a Faraday rotation of 40.5 degrees were observed, giving a figure of merit, obtained as the quotient of the observed rotation and the insertion loss, of 1000 degrees per decibel for the rod in question. The intensity of magnetization (4IIM) for the material at saturation was 2960 gauss.

Example 2

A tapered ferrite rod 2.5 inches in length and 0.160 inch in diameter was machined from a material prepared by the method described in Example 1, except that the second calcination there described was accomplished at 900° C. for the material herein, rather than at 1000° C. as in Example 1.

The ferrite, prepared from 107 grams of nickel carbonate, 12.4 grams of copper carbonate, 152 grams of ferric oxide and 2.30 grams of manganese carbonate has a metal content which may be specified as:

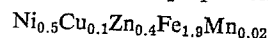


where the proportions are given in terms of gram atoms of metal present. Measurements were made on the rod, mounted in polyfoam in a $\frac{3}{4}$ inch diameter round waveguide section, at 11.2 kilomegacycles per second. An insertion loss of 0.04 decibel and a Faraday rotation of 57 degrees were found at a magnetic field intensity of 300 oersteds. The figure of merit was, thus, 1400 degrees per decibel.

The resistivity of the material was $2 \times (10^9)$ ohm-centimeters, and the intensity of magnetization (4IIM) at saturation was 2960 gauss.

Example 3

A material whose metallic constituents, in terms of gram atoms, were present in the proportions

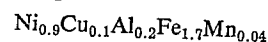


was prepared from 59.3 grams of nickel carbonate, 12.4 grams of copper carbonate, 32.5 grams of zinc oxide, 152 grams of ferric oxide and 2.30 grams of manganese carbonate.

A tapered rod 3.4 inches long and 0.140 inch in diameter was machined from the material, prepared by the method described in Example 2 above. The rod, with a density of 5.3 grams per cubic centimeter and a resistivity of 2×10^9 ohm-centimeters, was mounted in "polyfoam" in a hollow waveguide with an inside diameter of $\frac{7}{8}$ inch. At a magnetic field intensity of 300 oersteds the ferrite showed a Faraday-rotation of 47 degrees and an insertion loss of 0.09 decibel giving a figure of merit of 520 degrees per decibel. The intensity of magnetization (4IIM) at saturation was 4800 gauss for this sample.

Example 4

Starting with 107 grams of nickel carbonate, 12.4 grams of copper carbonate, 15.6 grams of aluminum hydroxide, 136 grams of ferric oxide, and 4.60 grams of manganese carbonate, a ferrite containing metals in the following proportions, in terms of gram atoms of the constituents, was prepared:

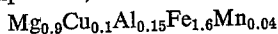


The preparative method followed the details of Example

2. The resultant ferrite had a resistivity of 2×10^9 ohm-centimeters, an intensity of magnetization (4IM) at saturation of 1900 gauss, and a density of 5.15 grams per cubic centimeter. When measured at a frequency of 9.6 kilomegacycles per second under conditions similar to those given in Example 3, a figure of merit comparable to that in Example 3 was observed.

Example 5

A ferrite composition,

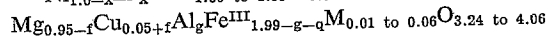
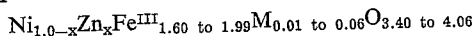


the subscripts signifying the metal proportions in terms of gram atoms, was prepared according to the detailed procedure of Example 2 from the following starting materials: magnesium carbonate, 75.8 grams; copper carbonate, 12.4 grams; aluminum hydroxide, 11.7 grams; ferric oxide, 128 grams; and manganese carbonate, 4.60 grams.

The resultant material showed a resistivity of 2×10^{10} ohm-centimeters and had a density of 4.4 grams per cubic centimeter. The intensity of magnetization (4IM) of the material at saturation was 1700 gauss.

What is claimed is:

1. A high resistivity ferrite material having a resistance of at least 2×10^9 ohm centimeters selected from the group consisting of ferrite materials having the following compositions:



where the values of the variable subscripts are bounded as follows:

x is bounded between 0 and 0.45,

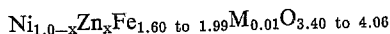
f is 0.05

g is bounded between 0.05 and 0.7,

q is bounded between 0.1 and 0.25,

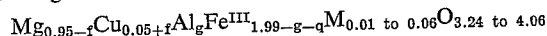
and M is at least one element selected from the group consisting of cobalt and manganese, said ferrite materials being the reaction product formed by shaping an oxide mixture of initial ingredients under pressure and firing said shaped mixture in an oxidizing atmosphere at a temperature of 1050°C . to 1350°C .

2. The high resistivity ferrite material of claim 1 having the following composition:



where x is bounded between 0 and 0.45, and M is at least one element selected from the group consisting of cobalt and manganese.

3. The high resistivity ferrite material of claim 1 having the following composition:



where

f is 0.05,

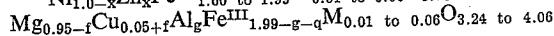
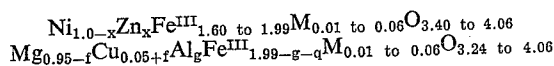
g is bounded between 0.05 and 0.7,

q is bounded between 0.10 and 0.25,

and M is at least one element selected from the group consisting of cobalt and manganese.

4. In a microwave transmission system, a device comprising at least one waveguide and a gyromagnetic ferrite body subjecting waves in the 300 megacycle per second to 50,000 megacycle per second frequency range transmitted therethrough to a Faraday rotation, said ferrite body having the composition of claim 1.

5. In a microwave transmission system, a device comprising at least one waveguide and a gyromagnetic ferrite material subjecting waves in the 300 megacycle per second to 50,000 megacycle per second frequency range transmitted therethrough to a Faraday rotation, said ferrite material being selected from the group consisting of ferrite materials having the following compositions:



where the values of the variable subscripts are bounded as follows:

x is bounded between 0 and 0.45,

f is bounded between 0.05 and 0.25,

g is bounded between 0.05 and 0.7,

q is bounded between 0.1 and 0.25,

and M is at least one element selected from the group consisting of cobalt and manganese, said ferrite materials being the reaction product formed by shaping an oxide mixture of initial ingredients under pressure and firing said shaped mixture in an oxidizing atmosphere at a temperature of 1050°C . to 1350°C .

References Cited in the file of this patent

UNITED STATES PATENTS

1,976,230	Kato et al. -----	Oct. 9, 1934
2,576,456	Harvey et al. -----	Nov. 27, 1951
2,644,930	Luhrs -----	July 7, 1953
2,685,568	Wilson -----	Aug. 3, 1954
2,719,274	Luhrs -----	Sept. 27, 1955
2,723,239	Harvey -----	Nov. 8, 1955
2,736,708	Crowley -----	Feb. 28, 1956
2,860,105	Gorter et al. -----	Nov. 11, 1958

FOREIGN PATENTS

Great Britain -----	Oct. 27, 1954
Great Britain -----	Jan. 12, 1955
France -----	Mar. 18, 1953
France -----	June 2, 1954
France -----	Aug. 11, 1954

OTHER REFERENCES

- 55 Weil: Comptes Rendus, vol. 234, pp. 1351, 1352 (1952).