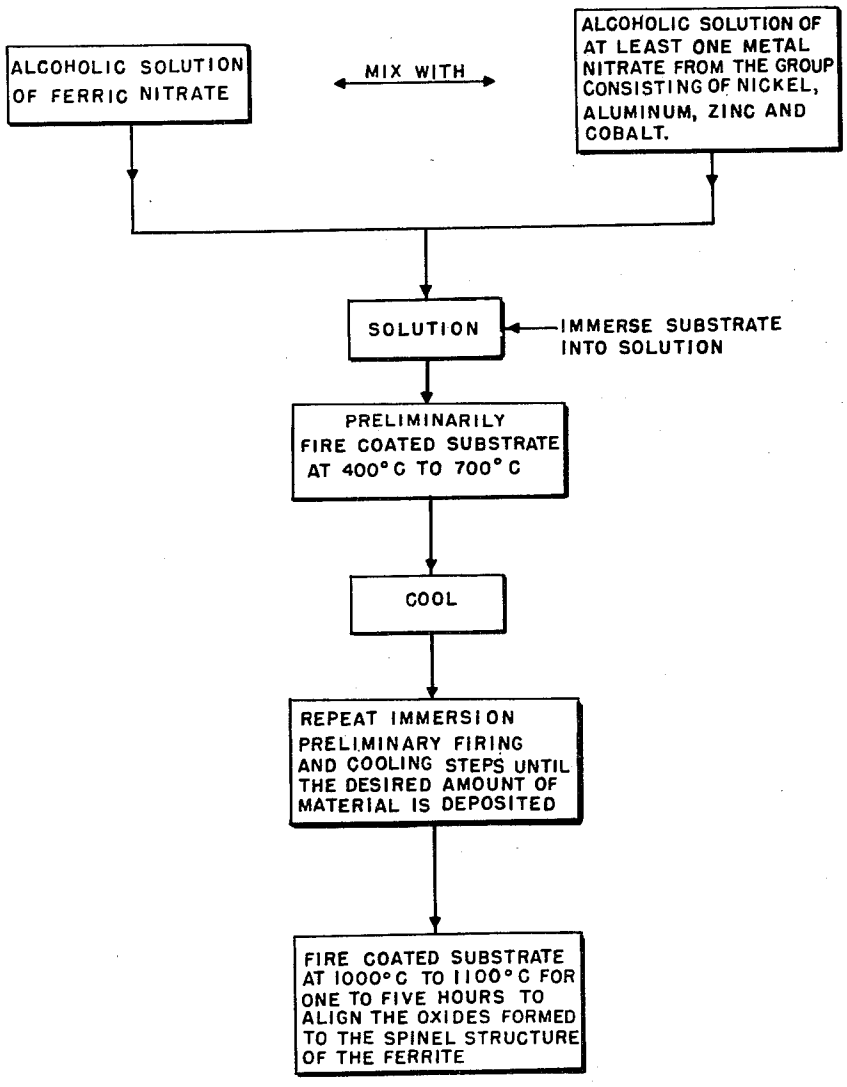
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METHOD OF COATING A SUBSTRATE WITH MAGNETIC FERRITE FILM

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METHOD OF COATING A SUBSTRATE WITH MAGNETIC FERRITE FILM

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The invention described herein may be manufactured and used by or for the Government for governmental purposes, without the payment of any royalty thereon.

This application is a continuation-in-part of my U.S. patent application Serial Number 99,963 filed March 31, 1961, now abandoned, for method of making Magnetic Ferrite Film. This invention relates to a simple method of making magnetic ferrite films from nitrate solution.

An object of the invention is to make magnetic ferrite films of high compositional purity by a relatively short and simple technique.

Magnetic ferrite films are relatively new. They are adaptable for use in computer memories, logic circuits, and microwave devices. One very promising application of the magnetic ferrite films is in the traveling-wave maser structure wherein their use provides for an unconditionally-stable maser amplifier. The use of magnetic ferrite films is of distinct advantage over the use of bulk ferrite in microwave devices at high frequencies. This is because one cannot grind solid ferrite materials thin or uniform enough to fit into such devices. The magnetic ferrite films on the other hand are suitable in these devices as they can be coated to any thickness and be cut to any desired shape. Alternatively, the films can be of economic advantage in that the substrate can be cut to the desired shape beforehand and then coated.

Heretofore, many of these films have been made by the vacuum deposition technique of vaporizing the metals on suitable substrates and then heating or rather firing the metals at high temperatures for prolonged periods to convert the metals to oxides and alignment to the ferrite film.

It has now been found that magnetic ferrite films of high compositional purity can be made by a relatively short and simple technique. The technique involves the dissolving of ferric nitrate and one or more nitrates of the metals of the group of magnesium, nickel, aluminum, zinc, and cobalt in alcohol at room temperature; immersing the surface of a substrate in the solution; preliminary firing the coated substrate at 400° C. to 700° C. in a furnace; and succesively cooling to room temperature between coats. After weighing on a balance to determine exact amounts of material deposited, the coated substrate is heated to 1000° C. to 1100° C. in a furnace for one to five hours to align the oxides formed to the spinel structure of the ferrite.

A flow sheet of the process is illustrated by the drawing.

Some preferred embodiments of the invention are hereinafter described.

Example 1

Nickel nitrate is reacted with ferric nitrate in such amounts that one mole is present for two moles of iron according to the reaction

$$Ni(NO_3)_2 + 2Fe(NO_3)_3 \xrightarrow[C_2H_5OH]{\text{heat}} NIFe_2O_4$$

According to the method, 86 grams (0.3 mole) of $Ni(NO_3)_2.6H_2O$ and 86 grams (0.2 mole) of $Fe(NO_3)_3.9H_2O$ are separately dissolved in 100 milliliters of anhydrous ethanol, the metal concentration of these solutions being 0.1735 gram and 0.1189 gram of nickel and iron, respectively per milliliter of solution. A stoichiometric ratio of the above-mentioned stock solutions is prepared by mixing 25 milliliters of the iron solution containing 2.9725 grams of iron with 9.02 milliliters of nickel solution containing 1.5651 grams of nickel. A fused quartz substrate is then dipped in the stoichiometric alcoholic nitrate solution allowing the excess to flow back. The substrate is then placed in a furnace set at 500° C. for 60 to 90 seconds, removed, and then cooled to room temperature. During this preliminary heating, nitric oxide fumes evolve causing flaking of the material at varied spots upon the surface of the fused quartz. The flakes are gently removed and the substrate redipped in the solution repeating the above-mentioned procedure until an even coat of a desired thickness is obtained. Between 0.5 and 1.0 milligram of material is deposited during each operation. The substrate is then fired at 1000° C. for one hour to align the metallic oxides formed (that is, NiO and Fe_2O_3) to the spinel structure of the ferrite. X-ray diffraction techniques carried out on the coated substrate indicate that the deposited coating corresponds to a nickel ferrite spinel structure.

An evaluation of the magnetic properties of the nickel ferrite films at microwave frequencies is then made. In the evaluation, microwave measurements are made on films deposited on quartz and alumina substrates having the dimensions 0.9" x 0.4" plotting attenuation versus applied field. The resulting absorption curves show a definite activity at microwave frequencies and portray the films as being ferromagnetic.

Example 2

Magnesium nitrate is reacted with ferric nitrate in such amounts that one mole of magnesium is present for two moles of iron according to the reaction

$$Mg(NO_3)_2 + 2Fe(NO_3)_3 \xrightarrow[C_2H_5OH]{\text{heat}} MgFe_2O_4$$

According to the method, magnesium and iron stock solutions are prepared by dissolving 43 grams (0.11 mole) of $Fe(NO_3)_3.9H_2O$ in 50 milliliters of anhydrous ethanol and 43 grams (0.17 mole) of $Mg(NO_3)_2.6H_2O$ in 50 milliliters of anhydrous ethanol. The metal concentration of these solutions upon analysis is 0.0529 gram of iron per milliliter of solution. A stoichiometric ratio of the above-mentioned stock solutions is prepared by mixing 15 milliliters of the iron solution containing 1.2345 grams of iron with 5.0 milliliters of magnesium solution containing 0.2645 gram of magnesium. The remaining technique of obtaining the ferrite film is the same as in Example 1. X-ray diffraction techniques carried out on the coated substrate indicate that the deposited coating corresponds to a magnesium ferrite spinel structure.

An evaluation of the magnetic properties of the magnesium ferrite films at microwave frequencies is then made. In the evaluation, microwave measurements are made on films deposited on quartz and alumina substrates having the dimensions 0.9" x 0.4" plotting attenuation versus applied field. The resulting absorption curves show a

definite activity at microwave frequencies and portray the films as being ferromagnetic.

The evaluation of the magnetic properties of the nickel ferrite and magnesium ferrite films prepared in Examples 1 and 2 as measured at microwave frequencies (X-band) is shown in the following table:

Material	Film Thickness (Microns)	Amount Deposited (Milligrams)	Resonant Frequency (mc.)	Resonant Applied Field (Oersteds)	Linewidth (Oersteds)
$NiO.Fe_2O_3$	22.86	28.30	9,091	1775	2,625
$NiO.Fe_2O_3$	15.36	19.00	9,087	1775	2,375
$NiO.Fe_2O_3$	7.47	9.30	9,092	2600	1,500
$MgO.Fe_2O_3$	20.1	27.7	9,514	2700	2,250
$MgO.Fe_2O_3$	19.5	27.0	9,518	2575	1,950

Example 3

Magnesium nitrate is reacted with aluminum nitrate and ferric nitrate in such amounts that one mole of magnesium is present for every 0.4 mole of aluminum for every 1.6 mole of iron according to the reaction

$$Mg(NO_3)_2 + 0.4Al(NO_3)_3 + 1.6Fe(NO_3)_3 \xrightarrow[\text{ethanol}]{\text{heat}} Mg(0.4Al.1.6Fe)O_4$$

According to the method, magnesium nitrate, aluminum nitrate, and iron nitrate stock solutions are prepared by dissolving 43 grams (0.11 mole) of $Fe(NO_3)_3.9H_2O$ in 50 milliliters of anhydrous ethanol, 43 grams (0.17 mole) of $Mg(NO_3)_2.6H_2O$ in 50 milliliters of anhydrous ethanol, and an undetermined amount of $Al(NO_3)_3.9H_2O$ in 50 milliliters of anhydrous ethanol. A stoichiometric ratio of the above-mentioned stock solutions is prepared by mixing 15 milliliters of the iron solution containing 1.9575 grams of iron with 10.07 milliliters of magnesium solution containing 0.5328 gram of magnesium with 11.20 milliliters of aluminum solution containing 0.2364 gram of aluminum. A 96 percent alumina substrate is then dipped in the stoichiometric alcoholic nitrate solution allowing the excess to flow back. The substrate is then placed in a furnace set at 500° C. for 60 to 90 seconds, removed, and then cooled to room temperature. During this preliminary heating, nitric oxide fumes evolve causing flaking of material at varied spots upon the surface of the alumina. The flakes are gently removed and the substrate redipped in the solution repeating the above-mentioned procedure until an even coat of a desired thickness is obtained. Between 0.5 and 1.0 milligram of material is deposited during each operation. The substrate is then fired at 1100° C. for 1½ to 5 hours to align the metallic oxides formed (that is, MgO and $0.4Al.1.6FeO_3$) to the spinel structure of the ferrite. X-ray diffraction techniques carried out on the coated substrate indicate that the deposited coating corresponds to a magnesium aluminum ferrite structure of the formula $Mg(0.4Al.1.6Fe)O_4$.

An evaluation of the magnetic properties of the magnesium aluminum ferrite films at microwave frequencies is then made. In the evaluation, microwave measurements are made on films deposited on 96 percent alumina substrates having the dimensions 0.9" x 0.4" plotting attenuation versus applied field. The resulting absorption curves show a definite activity at microwave frequencies and portray the films as being ferromagnetic. The evaluation of the magnetic properties of the magnesium aluminum ferrite films prepared in Example 3 as measured at microwave frequencies (X-band) is shown in the following table:

Material	Film Thickness (Microns)	Resonant Frequency (mc.)	Resonant Applied Field (Oersteds)	Linewidth (Oersteds
$MgO.0.4Al.1.6FeO_3$	22.5	9,375	3,350	900
$MgO.0.4Al.1.6FeO_3$	22.5	9,370	3,200	900
$MgO.0.4Al.1.6FeO_3$	22.5	9,380	2,975	750

Example 4

Magnesium nitrate is reacted with zinc nitrate and iron nitrate in such amounts that one-half mole of magnesium is present for every one-half mole of zinc for every two moles of iron according to the reaction

$$0.5Mg(NO_3)_2 + 0.5Zn(NO_3)_2 + 2Fe(NO_3)_3 \xrightarrow[\text{ethanol}]{\text{heat}} (0.5Mg.0.5Zn)Fe_2O_4$$

According to the method, magnesium nitrate, zinc nitrate, and iron nitrate stock solutions are prepared by dissolving 43 grams (0.17 mole) of $Mg(NO_3)_2.6H_2O$ in 50 milliliters of anhydrous ethanol, an undetermined amount of $Zn(NO_3)_2 \cdot 6H_2O$ in 50 milliliters of anhydrous ethanol, and 43 grams (0.11 mole) of $Fe(NO_3)_3.9H_2O$ in 50 milliliters of anhydrous ethanol. A stoichiometric ratio of the above-mentioned stock solutions is prepared by mixing 11.9 milliliters of the iron solution containing 1.5520 grams of iron with 3.19 milliliters of the magnesium solution containing 0.1689 gram of magnesium and 2.97 milliliters of the zinc solution containing 0.4542 gram of zinc. The remaining technique of obtaining the ferrite film is the same as in Example 3. X-ray diffraction techniques carried out on the coated substrate indicate that the deposited coating corresponds to a magnesium zinc ferrite spinel structure of formula $(0.5Mg.0.5Zn)Fe_2O_4$.

An evaluation of the magnetic properties of the magnesium zinc ferrite film at microwave frequencies (X-band) is then made. In the evaluation, microwave measurements are made on a film 22.5 microns in thickness deposited on an alumina substrate having the dimensions 0.9" x 0.4" plotting attenuation versus applied field. According to the evaluation, the film is found to have a resonant frequency of 9381 megacycles, a resonant applied field of 2450 oersteds, and a linewidth of about 875 oersteds. This indicates definite activity at microwave frequencies and portrays the film as being ferromagnetic.

The alcohol solvent recited in the statement of the invention and disclosed in Examples 1, 2, 3, and 4 above is preferred as the dispersing agent or carrier. That is, it gives proper flow tendencies to the film forming solution of metallic nitrates. Other solvents that aid in evaporation and dispersion of the nitrates could be used in its place, as for example, a hydrocarbon solvent or a lower ketone. In no instance, it should be pointed out, is there a reaction between the metallic nitrate and the particular dispersing agent or carrier selected. Thus, for example, a metallic alcoholate is not formed when carrying out the method.

A practical variation in the method is to initially melt the metallic nitrate and then to add just enough water to it to maintain a liquid state. The particular dispersing agent selected can then be added to stoichiometric ratios of the stable aqueous stock solution at the time of carrying out the method. Though this technique is not necessary to the invention, it is of distinct advantage where the solution resulting from the dispersion of the metallic nitrate directly in the alcohol would be unstable after three to four days, as for example, in the case of ferric nitrate.

Example 5

Nickel nitrate is reacted with zinc nitrate and iron nitrate in such amounts that 0.75 mole of nickel is present for every 0.25 mole of zinc for every 2 moles of iron according to the reaction

$$0.75Ni(NO_3)_2 + 0.25Zn(NO_3)_2 + 2Fe(NO_3)_3 \xrightarrow[\text{methanol}]{\text{heat}} (0.75Ni.0.25Zn)Fe_2O$$

According to the method, stock solutions of

$Fe(NO_3)_3.9H_2O$, $Ni(NO_3)_2.6H_2O$, and $Zn(NO_3)_2.6H_2O$

are first prepared by heating 135 grams of each metallic nitrate to liquefaction without causing decomposition.

The now liquified metallic nitrates are kept in the liquid state by the addition of 70 milliliters of distilled water. The stock solutions remain constant in concentration for an indefinite period. A stoichiometric ratio of these stock solutions is then measured out by mixing 30 milliliters of the iron solution containing 3.8130 grams of iron with 7.26 milliliters of the nickel solution containing 1.5026 grams of nickel and 2.13 milliliters of the zinc solution containing 0.5581 gram of zinc. Methanol is then added to the resulting stoichiometric solution in any desired amount depending on one's observation as to the thickness of deposition on the substrate being coated. A 96 percent alumina and a fused quartz substrate are then separately dipped in the stoichiometric aqueous alchoholic nitrate solution allowing the excess to flow back. The remaining technique of obtaining the ferrite films is the same as in Example 3. X-ray diffraction techniques carried out on the coated substrate indicate that the deposited coating corresponds to a nickel zinc ferrite spinel structure of the formula

$$(0.75Ni.0.25Zn)Fe_2O_4$$

An evaluation of the magnetic properties of the nickel zinc ferrite films at microwave frequencies is then made. In the evaluation, microwave measurements are made on films deposited on fused quartz and 96 percent alumina substrates having the dimensions 0.9" x 0.4" plotting attenuation versus applied field. The resulting absorption curves shown a definite activity at microwave frequencies and portray the films as being ferromagnetic. The evaluation of the magnetic properties of the nickel zinc ferrite films prepared in Example 5 as measured at microwave frequencies (X-band) is shown in the following table:

Material	Film Thickness (Microns)	Resonant Frequency (mc.)	Resonant Applied Field (Oersteds)	Linewidth (Oersteds)
$(0.75Ni.0.25Zn)Fe_2O_4$	22.5	9,210	2,000	1825
$(0.75Ni.0.25Zn)Fe_2O_4$	22.5	9,378	1,700	650
$(0.75Ni.0.25Zn)Fe_2O_4$	22.5	9,378	1,650	675
$(0.75Ni.0.25Zn)Fe_2O_4$	22.5	9,374	1,600	650
$(0.75Ni.0.25Zn)Fe_2O_4$	22.5	9,384	1,600	580
$(0.75Ni.0.25Zn)Fe_2O_4$	22.5	9,372	1,565	795

The preliminary heating in Examples 1 through 5 above can be effected with the aid of a hot plate set on high. In such a case as is also true in Examples 1 through 5 above, both sides of the substrate are covered but only one is needed for evaluation. Therefore, one side is removed of its coating with acid or a razor blade.

The substrate used is not critical; all that is required is that it be temperature stable up to 1100° C. Alumina and fused quartz have been found to be most useful as the substrate.

In the aforementioned examples, the thickness of the coated substrate is determined by weighing out prescribed amounts of deposited material on the selected substrate, the selected substrate having a definite specified area. The substrate thickness is measured before and after deposition of the coating with a sensitive instrument such as an electronic micrometer. The calculated film thickness is then correlated with the weight of material deposited on the specified area. Once a correlation is made, only a deposited weight is required over a specified area.

In carrying out the method, the ratio in which the metallic nitrates can be reacted can be varied depending on the ionic radius of the metals, the valence of the metals, and the crystal structure of the ferrite itself.

It is intended that the foregoing description be considered merely as illustrative and not in limitation of the invention as hereinafter claimed.

What is claimed is:

1. The method of coating a substrate with magnetic ferrite film of about 7 to 23 microns in thickness comprising mixing an alcoholic solution of ferric nitrate with an alcoholic solution of at least one nitrate of a metal selected from the group consisting of nickel, aluminum, zinc, and cobalt in the stoichiometric proportion necessary to form the ferrite, immersing a substrate that is thermally stable up to 1100° C. into the thus prepared solution, preliminary firing the coated substrate at 400° C. to 700° C., cooling the coated substrate, repeating the immersion, preliminary firing and cooling steps until the desired amount of magnetic ferrite material is deposited in situ on the substrate, and firing the coated substrate at 1000° C. to 1100° C. for one to five hours to align the oxides formed to the spinel structure of the ferrite.

2. The method of coating a substrate with magnetic ferrite film according to claim 1 wherein the alcoholic solution of ferric nitrate is mixed with alcoholic solution of nickel nitrate and zinc nitrate.

3. The method of coating a substrate with magnetic ferrite film according to claim 1 wherein the alcoholic solution of ferric nitrate is mixed with alcoholic solution of nickel nitrate.

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