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MAGNETIC CORE AND METHOD FOR
MANUFACTURING SAMEGodshalk Berge, Chicago, Ill., assignor to Aladdin
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This invention relates to magnetic cores for use in inductance tuning coils, and it relates particularly to the composition and to the method for producing magnetic cores which operate efficiently in resonant circuits in the high frequency television and FM range of about 76.5 to 108 mc.

The characteristics of a magnetic core are often measured by the frequency range, Q factor and the thermal drift of the core within the frequency of its intended use. Empirically, it has been shown that compositions suitable for use in circuits in the radio frequency or broadcast range may not be equally suitable for use in circuits operating at higher frequencies, such as the ultra high frequency FM and the television ranges. The characteristic most often affected by the increased frequency is the Q value, which may fall to an unusable low value even as a result of a minor increase in frequency.

Optimum conditions are achieved when the magnetic core has the following characteristics, Q in excess of 80, thermal drift which is less than 0.01 percent degree centigrade, and range of the desired magnitude in the frequency band for which it is intended.

It is an object of this invention to provide a magnetic core and a method for manufacturing the same from commercially available raw materials for use in electrical circuits, especially in the television and FM range.

Another object is to provide a magnetic core that has the characteristics of high Q, low thermal drift and satisfactory range within the high frequency bands of 76 to 108 mc.

A further object is to provide a new method for producing magnetic cores for use in circuits, operating in these very high frequency ranges, which method includes the combination of commercially available raw materials to produce stable magnetic compounds and the combination of these compounds in various proportions, with and without modifying substances to form the final product.

I have found that the characteristics of a magnetic core may not depend entirely upon the raw materials and the elements of which it is formed, but important also is the arrangement which those elements assume in the final product. I have found that certain metal oxides when compounded together develop magnetic properties, and in their compounded form contribute materially to the desirable characteristics secured in cores forming the subject matter of this invention. I have found further that these oxides should be formed to stable compounds

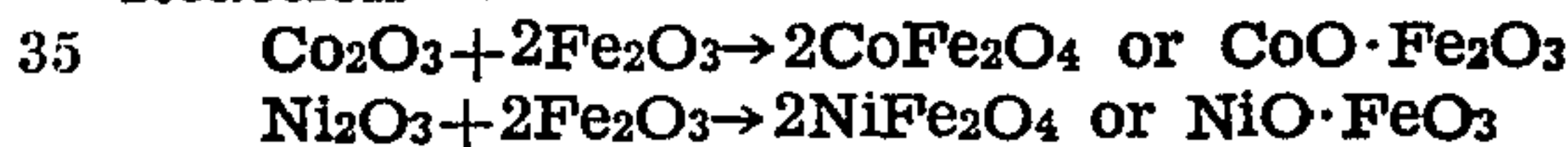
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and that the amounts and types of additives should be closely controlled; otherwise, the composition of the compounds will be altered either by chemical reaction or by displacement with more active elements, whereupon the effect of the materials present is greatly minimized.

For example, a core formed by reaction in combination of iron oxide (Fe_2O_3), cobalt oxide (Co_2O_3), nickel oxide (Ni_2O_3), zinc oxide (ZnO), vanadium oxide (V_2O_5), and magnesium zirconate (MgZrO_3) does not have characteristics comparable to a magnetic core formed from the same materials having a molecular arrangement of the type secured by my invention. When practicing my invention with the above materials, the final product is a magnetic core having a frequency range of 108 to 76.5 mc., a Q of 90 which remains practically constant over the entire range, and an exceptionally low thermal drift of about 0.004 percent degree centigrade.

An important feature of my invention resides in the formation of stable salts of the cobalt or nickel components by the separate reaction of the cobalt or nickel oxides in sufficient amount to form what is believed to be the corresponding cobalt or nickel ferrites. The amount of material employed for carrying out the invention may most easily be designated in terms of molecular equivalents since two molecular weights of iron oxide appear to thermally react with one molecular weight of the cobalt or nickel oxides in the formation of the corresponding salts according to the following formulae:

Reaction



Strict adherence to amounts determined on the basis of molecular equivalents is not essential because acceptable results can be secured by variation of one or the other of the oxides by about 10 per cent from the theoretically calculated amount.

In specific application, the oxide of iron in finely divided form is mixed with the oxide of cobalt or the oxide of nickel in finely divided form and the mass is fired for about two hours at 2200° F. The time of firing might be varied according to the temperature employed and the mass to be reacted. For example, proper firing may require 3 to 4 hours at 2000° F., while 1 hour or less may suffice when reaction is carried out at a temperature of 2500° F. The reaction product, when cooled to room temperature, is a hard friable mass having magnetic properties,

and for further processing into magnetic cores, it is reduced to finely divided form.

Although magnetic cores might be formed of the finely divided reaction products of nickel oxide with iron oxide, or of cobalt oxide with iron oxide, I prefer to combine the two reaction products in substantially equal proportions or with one in excess of the other up to about 25 percent. Core formation is effected by a molding operation followed by a heat treatment to a temperature of about 1800 to 2350° F. for about 1 or more hours. Best results are secured when the heat treated cores are gradually cooled to room temperature at a rate, for example, of about 100° F. per hour. My invention is not limited to the above described conditions since the time of heat treatment may vary according to the temperature used and the rate of cooling is influenced by the mass of material involved.

Temporary cohesive strength is imparted to the molded product prior to heat treatment by the admixture of a small amount of resinous binder which may include the reaction products of phenol-aldehydes, urea-aldehydes, vinylpolymers and copolymers, polyacrylates, polystyrene, and the like. Up to 10 percent binder may be used, however, 2 to 3 percent ordinarily is sufficient. The described binders are heat sensitive and are subject to thermal decomposition as the temperature of heat treatment exceeds 500° F., whereupon the greater portion of the bonding action secured thereby is lost and reliance is had upon the development of a bond by one or more of the metallic substances making up the core composition, which bond is usually developed at higher temperatures.

Although magnetic cores can be produced solely from the reaction products of the oxides of cobalt and nickel with iron oxides, zinc oxide may be added to extend the frequency range which is obtained by means of the cores, especially when used in amounts corresponding to less than 15 percent by weight of the final product.

To prevent unstabilization of the core ingredients formed by reaction of cobalt oxides and nickel oxides with iron oxide, such as by displacement of either the nickel or cobalt atom by the more basic zinc atom, sufficient additional iron oxide should be incorporated in the mix to neutralize the zinc oxide. The addition of zinc oxide and corresponding amounts of iron oxide to the described reaction products might be made during the core forming process, but in many instances, best results are secured when the added substances are first reacted at firing temperature corresponding to those previously described to effect the formation of a neutral salt, believed to be zinc ferrite. Zinc oxide and iron oxide combine in substantially equi-molecular proportions and, therefore, it is expedient to designate the amounts that may be added in such terms, it being understood that variations of about 10 percent from theoretically calculated amounts are permissible. Although it is undesirable to disturb the neutral salts of cobalt and nickel, a small amount of displacement by zinc may be unavoidable under the conditions employed in the heat treatment.

Further improvement in the properties of a manufactured magnetic core is secured by the addition, previous to molding, of a small amount of vanadium oxide to the ingredients from which the core is manufactured. Vanadium oxide functions chiefly to expand the frequency range ob-

tained with the core and for this purpose, amounts up to 5 percent by weight of the core composition have been successfully used. The improvement secured by further additions does not warrant the added cost of vanadium oxide and, therefore, I prefer to limit my use to less than 10 percent.

During heat treatment, it appears that a stable salt is formed by reaction of vanadium oxide with iron oxide, the major reaction product, possibly being ferro-vanadinite. To bring about this reaction, sufficient additional iron oxide is added, or else is allowed to remain unneutralized in the previously described reaction products.

A very important feature of this invention resides in the use of magnesium zirconate in the core compositions previously described. Importance is directed to the addition of magnesium zirconate because it has the novel and very desirable characteristic of substantially reducing the thermal drift while supporting the Q values of the compounded materials. Magnesium zirconate is effective when used in amounts up to 12 percent by weight of the composition, and best use is made when used in amounts ranging from 4 to 8 percent. The same effect on thermal drift cannot be secured by the addition of other commonly used materials, such as zirconium oxide, magnesium titanite, strontium titanite, or calcium stannite. When used in designated amounts, magnesium titanite can be substituted in part with about 25 percent by weight lead titanite.

It will be manifest that the materials set forth may be formulated together within the weight limitations prescribed to secure magnetic cores having excellent characteristics with respect to range, Q, and thermal drift, in television or FM circuits. It will be understood that these same compositions might also be used in lower frequency circuits such as radio frequencies and the like. The additive materials may be compounded with the separate thermal reaction products formed of cobalt and nickel and zinc oxides with iron oxide, and with zinc oxide, unless previously separately reacted with iron oxide, and then molded to core formation followed by heat treatment under the conditions previously described. With these materials in the desired arrangement, inequalities in density which normally follow molding under high pressure, are compensated by unequal shrinkage during heat treatment to the extent that a magnetic core is secured having substantially equal permeability throughout.

The following examples given by way of illustration, but not by way of limitation, describe the manufacture of magnetic cores in accordance with this invention.

EXAMPLE 1

Materials

56 percent iron oxide (Fe_2O_3)
10 percent cobalt oxide (Co_2O_3)
8 percent nickel oxide (Ni_2O_3)
13 percent zinc oxide (ZnO)
5 percent vanadium oxide (V_2O_5)
8 percent magnesium zirconate (MgZrO_3)

Cobalt oxide and nickel oxide are separately mixed with about two molecular equivalents of iron oxide and fired at a temperature of about 2050° F. for 3½ hours. Upon cooling to room temperature, the friable reaction products are subdivided to a powdery state, intimately mixed

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with the other ingredients, and compounded with about 2 to 5 percent "A" stage phenol formaldehyde resin dissolved in alcohol medium. The composite mass is molded to core shape under about 2000 pounds per square inch pressure and then heat treated for about two hours at 2000° F. The heat treated core is cooled to room temperature by decrements of 100° per hour. The product has the following characteristics:

Range..... 108-76.5
Q..... 90
Thermal drift..... 0.004 percent per °C.

EXAMPLE 2

The amount of material employed is the same as that in Example 1 above. The cobalt oxide, nickel oxide and zinc oxide are separately mixed with the required molecular equivalents of iron oxide and fired at a temperature of about 2200° F. for about 1½ hours. When cooled to room temperature, the reaction products are subdivided to powdery form and mixed with the vanadium oxide, magnesium zirconate and the remaining iron oxide. To this mixture about 2.5 percent by weight phenol formaldehyde resinous binder are added and then it is molded to core formation. The molded product is subjected to heat treatment in the manner previously described in Example 1, except that the heat treatment is carried out at 2000° F. for 1½ hours. The characteristics of the resulting magnetic core correspond substantially with those secured by the use of the same elements in Example 1.

EXAMPLE 3

Materials

58 percent iron oxide
12 percent cobalt oxide
7 percent nickel oxide
12 percent zinc oxide
3 percent vanadium oxide
8 percent magnesium zirconate

The materials are reacted and combined in the manner described in connection with Example 1. The characteristics of the resulting product are as follows:

Range..... 78-108
Q..... 80
Thermal drift..... 0.004 percent per °C.

It will be manifest from the description that I have found a new and improved system relating to the reaction of materials to form salts and complexes which when compounded into cores with or without additives have material effect upon the characteristics of the magnetic core at relatively high frequencies. These same effects are not secured when the materials are not first reacted in the described manner to provide such compounds and complexes which it is desirable to have in unmodified form in the final product. To the best of my knowledge, no one before has deemed it desirable to form the magnetic core with products formed by the separate thermal reaction of nickel oxide and of cobalt oxide with iron oxide present in sufficient amounts to form a stable salt having magnetic properties. Although the addition of zinc oxide to various elements has previously been considered to extend the range of the core, no one before has found that it is important to control the addition of zinc oxide to minimize its effect upon the described reaction products. Importance is directed to the addition of magnesium zirconate

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which is effective drastically to reduce the thermal drift of these and other core compositions by amounts not heretofore contemplated.

It will be understood that the magnetic cores produced by the materials described in this invention find best use in the high frequency ranges but may also be advantageously used at lower frequencies. It will be further understood that numerous changes may be made in the amounts of materials, and the order of incorporation and the conditions under which they are reacted without departing from the spirit of the invention, especially as defined in the following claims.

I claim as my invention:

1. The method of manufacturing magnetic cores, comprising the steps of separately reacting Ni_2O_3 , Co_2O_3 and ZnO with Fe_2O_3 in the ratio of one equivalent weight of the nickel and cobalt oxides to about two equivalent weights of iron oxide and one molecular weight of zinc oxide to one molecular equivalent iron oxide at a temperature within the range of 2000-2500° F. for from 1-4 hours, compounding the reaction products in finely divided form with vanadium oxide and magnesium zirconate and a binder in amounts ranging up to 8 percent of the mix, molding the mix to mold shape, heat treating the molded mass at a temperature within the range of 1800-2200° F. for ½-2 hours, and then slowly cooling the heat treated mass to room conditions, the materials being incorporated in amounts ranging from 8-12 parts cobalt oxide, 6-12 parts nickel oxide, 5-15 parts zinc oxide, 1-10 parts vanadium oxide, 4-12 parts magnesium zirconate, and 40-65 parts iron oxide.

2. In the method of manufacturing magnetic cores, the steps of separately thermally reacting Ni_2O_3 , Co_2O_3 , zinc oxide and vanadium oxide with about two molecular equivalents of Fe_2O_3 per molecular equivalent of nickel oxide and cobalt oxide and one molecular equivalent of iron oxide per molecule of zinc oxide and vanadium oxide respectively at a temperature within the range of 2000-2500° F. for 1-4 hours, mixing the reaction products in finely divided form with the amount of the reaction product of zinc oxide and vanadium oxide being based upon a small amount up to about 15 percent zinc oxide and a small amount up to about 10 percent vanadium oxide based upon the mixture, molding the reaction product to core shape with less than 10 percent by weight of a temporary organic binder, and then heating the molded mass to a temperature between 1800-2350° F. for 1-2 hours.

3. In the method of manufacturing magnetic cores, the steps of separately thermally reacting Ni_2O_3 , Co_2O_3 , zinc oxide and vanadium oxide with about two molecular equivalents of Fe_2O_3 per molecular equivalent of cobalt and nickel oxide and one molecular equivalent of iron oxide per molecule of zinc oxide and vanadium oxide respectively at a temperature within the range of 2000-2500° F. for 1-4 hours, mixing the reaction products in proportions ranging from equal parts by weight to an excess of 25 percent by weight of the reaction product of nickel and cobalt oxide with iron oxide and a small amount up to about 15 percent by weight of zinc oxide as its reaction product and a small amount up to about 10 percent by weight of vanadium oxide as its reaction product with the reaction products in finely divided form and combined with up to 10 percent by weight of a temporary organic binder and 4-12 percent by weight of magnesium zirconate,

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molding the mass to core shape and then heating the molded mass to a temperature between 1800-2350° F. for at least ½ hour.

4. In the method of manufacturing magnetic cores, the steps of separately thermally reacting Ni_2O_3 and Co_2O_3 in the ratio of equal parts by weight to an excess of 25 percent by weight of one over the other with about two molecular equivalents of iron oxide at a temperature within the range of 2000-2500° F. for 1-4 hours, mixing the reaction products in finely divided form with a small amount up to about 10 percent by weight of a temporary organic binder, a small amount up to about 12 percent by weight of magnesium zirconate, a small amount up to about 15 percent by weight zinc oxide and a small amount up to about 10 percent by weight vanadium oxide with sufficient iron oxide to react with the zinc and vanadium oxides to form the corresponding ferrite, molding the mass to core shape and then heating the molded mass to a temperature between 1800-2350° F. for at least ½ hour.

5. The method of manufacturing magnetic cores, comprising the steps of mixing nickel ferrite and cobalt ferrite as major ingredients in the ratio of equal parts by weight to an excess of 25 percent by weight of one over the other with zinc ferrite in amounts less than 15 percent by weight calculated on the basis of zinc oxide, the thermal reaction product of vanadium and iron oxide present in amounts less than 10 percent by weight calculated on the basis of vanadium oxide, and less than 10 percent by weight of a temporary organic binder, molding the mixture to core shape and then heating the molded mass to a temperature within the range of 1800-2350° F. for about ½-2 hours.

6. The method of manufacturing magnetic cores, comprising the steps of mixing nickel ferrite and cobalt ferrite as major ingredients pres-

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ent in the ratio of equal parts by weight to an excess of 25 percent by weight of one over the other with zinc ferrite in amounts ranging up to 15 percent by weight calculated on the basis of zinc oxide, the thermal reaction product of vanadium and iron oxide in amounts ranging up to 10 percent by weight calculated on the basis of vanadium oxide, 4-12 percent by weight of magnesium zirconate and up to 10 percent by weight of a temporary organic binder, molding the mass to core shape and then heating the molded mass to a temperature within the range of 1800-2350° F. for about ½-2 hours.

7. A magnetic core formed by the method of claim 5.

8. A magnetic core formed by the method of claim 6.

9. A magnetic core as claimed in claim 8 in which magnesium zirconate may be substituted in amounts up to 25 percent by weight thereof by lead titanite.

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