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3,234,136

METHOD FOR PRODUCING SQUARE LOOP
NICKEL FERROUS FERRITE

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This invention relates to ferromagnetic material with a spinel structure and, in particular, to an improved nickel-ferrous ferrite having an excess of iron and characterized by an excitation response of a substantially square hysteresis, and to the method for making the same.

Ferrospinel ferrites are widely employed as magnetic memory elements and pulse transfer controlling devices in computer and data processing machines and in this application the degree of squareness of the hysteresis loop is desirably high for optimum performance.

Although extensive developments of square loop materials have been made in several chemically different ferrite systems, certain improvements are still desired. The high temperature coefficient of present ferrites precludes their use in applications where the temperature varies widely between read and write operations. With a temperature stable ferrite, memory systems could be used in adverse temperature environments which would not necessitate the employment of thermostatic controls.

A ferrite, which has come to recent attention in offering such a memory element, is the nickel-ferrous ferrite. It has been observed that the nickel-ferrous ferrite has a low temperature coefficient of coercive force. The desired squareness, in the ferrite, is obtained with a magnetic anneal after a sintering treatment. This requires that the ferrite be reheated after the sintering operation, and a field applied to the ferrite either by surrounding it with a solenoid or passing a wire through it. Although a magnetic anneal is used in some of the more recent

studies, some of the early work with ferrites does mention the development of squareness in nickel-ferrous ferrites without the use of a magnetic anneal. There the sintering was done in an atmosphere of carbon dioxide, nitrogen and hydrogen which may be classified as a protective atmosphere but which has to become more reducing as higher iron ferrites are used. That treatment demands a three component atmosphere which entails greater control than atmospheres which are most often desired in the production of ferrites.

Accordingly it is an object of this invention to provide an improved process for enhancing nickel-ferrous ferrites with squareness characteristics.

It is a further object of this invention to provide an improved square loop nickel-ferrous ferrite having a low temperature coefficient.

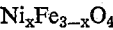
It is yet another object of this invention to provide a commercially feasible process for making square loop nickel-ferrous ferrites having an excess of iron therein.

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments thereof.

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From theoretical considerations and subsequent experimentation it has been discovered that low temperature coefficient square loop nickel-ferrous ferrites with an excess of iron therein are produced by sintering the required oxide constituents in an oxidizing atmosphere such as air. This is most surprising since it was previously thought that an excess of iron in a spinel in an oxidizing atmosphere would give rise to the formation of Fe_2O_3 , which usually separates out of the spinel as plates and prevents the development of squareness. In the fabrication of square loop materials, the formation of a second phase is generally undesirable.

It is found that a nickel-ferrous ferrite having the composition represented by the formula:



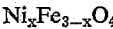
where x lies between 0.7 to 0.9 does have the ability to tolerate oxygen in its thermal formation and crystallization and provide a square loop ferrite. This entails sintering the required oxide mixture in an oxidizing atmosphere such as air at a temperature well within the area for the development of a single phase spinel, and, thereafter, cooling it to a lower temperature but one which is sufficiently high to maintain oxygen absorption.

With this procedure squareness and temperature stability are provided in the ferrite which is illustrated by the data in Table I. In Table I characteristics are given for temperature of -50° , 0° , $+40^\circ$ and 100° C. Noteworthy are the relatively unvarying peak times T_p , switching times T_s , and the high squareness ratio as measured by rV_1/wV_z . In this ratio rV_1 represents the read disturbed one signal and wV_z the write disturbed zero signal. In all instances the ratio is above 3 and, from practical consideration, it has been found that for use in an adverse temperature environment a ferrite must have a rV_1/wV_z ratio of at least 3 to 1.

TABLE I
[Pulse response of ferrite as a function of temperature under constant drive conditions; drive 1,000/500 ma., $t_r=0.2 \mu\text{sec.}$]

Temp. ($^\circ$ C.)	μV_1 (mv.)	rV_1 (mv.)	wV_z (mv.)	rV_1/wV_z	T_p (μ sec.)	T_s (μ sec.)	I_o (ma.)
100.....	118	108	16	6.75	0.30	0.60	510
40.....	99	92	13	7.10	0.30	0.67	548
0.....	78	76	13	5.87	0.32	0.70	615
-50.....	53	52	13	4.0	0.32	0.76	646

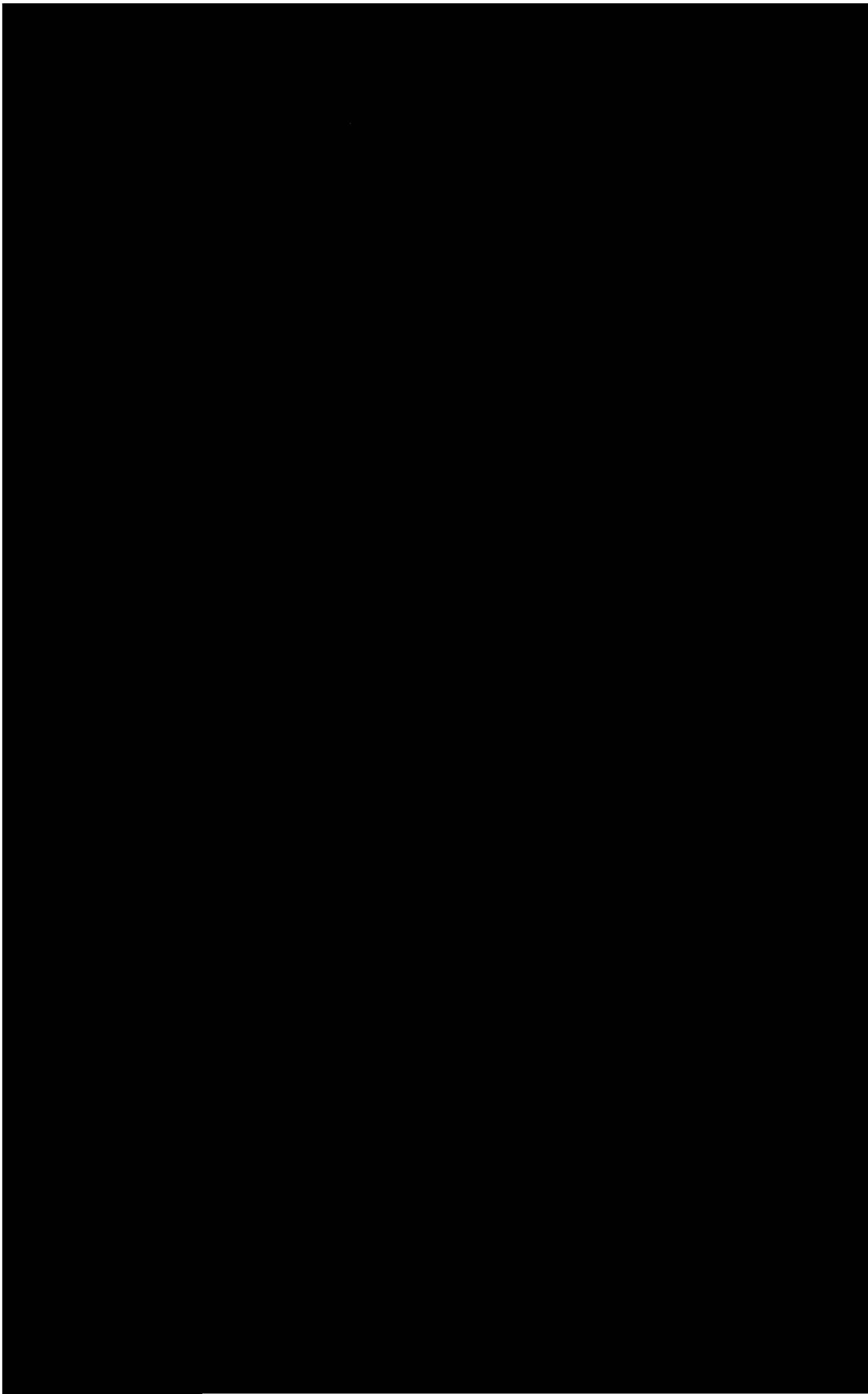
Now more specifically as to the procedures required in the present invention, mixes are blended which conform to the composition represented by the formula:



where x lies between 0.7 to 0.9.

Usual ceramic techniques are utilized in the present invention. Commercially pure fine particle oxides in the desired proportions are intimately mixed, for example, by wet ball milling to form a slurry. The slurry is thereafter dried and the dry cake subsequently ground to a fine powder.

The mixed raw materials are then calcined at a temperature varying between 800° C. to 1000° C. with it being preferable to calcine at about 900° C. The calcining is programmed such as to give a temperature rise of 45° to 48° per hour until the top temperature—the desired calcining temperature—is achieved. When the top temperature is achieved the material is soaked for one to one and one-half hours. It has been found that calcining temperatures below 800° C. develop pores while those above 1000° C. indicate secondary grain growth. The



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where the ferrite is formed from the mixture by a process which includes the steps of: heating the mixture in an oxidizing atmosphere in the range between 1420° C. to 1500° C., reducing the temperature about the heated mixture in an oxidizing atmosphere to a second temperature in the range between 1050° C. to 1250° C., and, thereafter, quenching the mixture to room temperature.

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