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PROCEDURE FOR PRODUCING A FERRITE, ESPECIALLY ADEQUATE  
FOR USE IN PULSE RELAY CORES  
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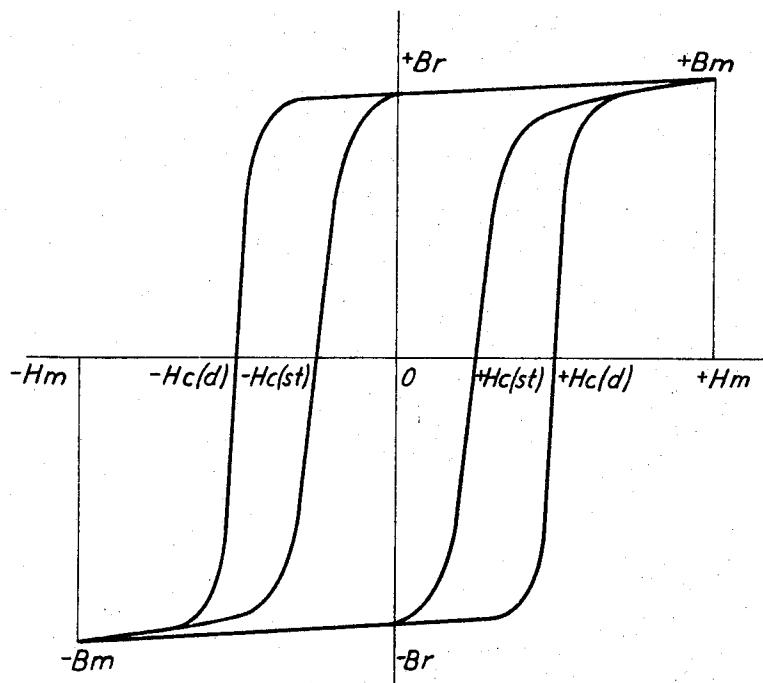


Fig. 1

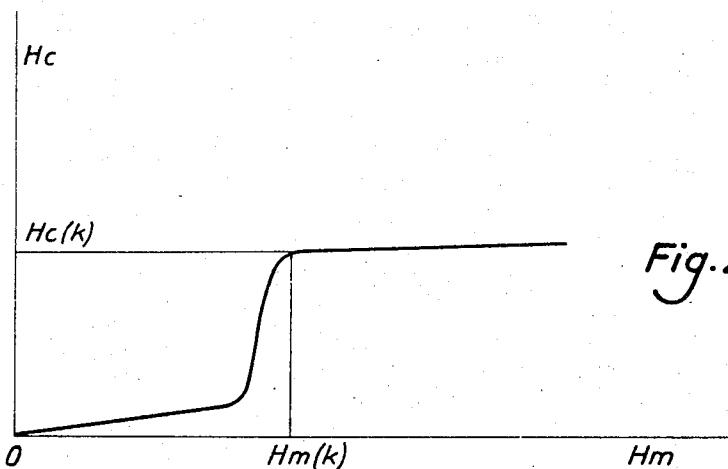


Fig. 2

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3,420,777

PROCEDURE FOR PRODUCING A FERRITE,  
ESPECIALLY ADEQUATE FOR USE IN PULSE  
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7 Claims

The development in automatic telephone switching progresses more and more towards electronically controlled switching. An important component of the switching systems is the pulse relay, i.e. a relay that may be operated and released by means of short current pulses. For the cores of these relays ferrite is used, which is a non-metallic material with two stable states of remanent magnetization. The material in question is manufactured by a ceramic process starting with a mixture of iron oxides and other adequate metal oxides. The mixture is pulverized and subjected to a preliminary sintering process, which includes heating to a temperature below the melting point of the metal oxides. After cooling the sintered material is again pulverized, a mould lubricant is added thereto and subsequently the mixture is moulded to desired form, for instance cores. The cores are subjected to a final sintering process by heating to a constant sintering temperature during a predetermined holding time, the sintering temperature also this time being below the melting point of the oxides.

The ferrite material to be adequate for pulse relay cores ought to have a high volume resistivity, a relatively high coercive force, a high remanent magnetization, and the hysteresis loop should be of substantially square form. At so-called dynamic magnetization, i.e. at pulse magnetization where maximum field force is applied within a few microseconds, the energy losses caused by the magnetic relaxation distortion should be small.

The known ferrites are principally of two different kinds, soft-magnetic and hard-magnetic, but neither of them fulfils all the mentioned requirements. The soft-magnetic ferrite often has a square hysteresis loop, but its coercive force is very low ( $0.1 \leq H_c \leq 3.0$ ). This material, therefore, is not adequate as a source of magnetic force or for the control of a sufficiently strong permanent magnetic field eventually used as a power source for a pulse relay.

The hard-magnetic material has a very high coercive force ( $H_c \geq 1000$ ) and cannot be used for pulse magnetization, because it requires too high amount of energy for magnetization.

The cobalt ferrite is a hard-magnetic ferrite, the coercive force of which may be lowered by the addition of certain non-magnetic materials, but this ferrite has a relatively low volume resistivity ( $< 10,000 \text{ ohm cm.}$ ), which is a great disadvantage. The pulse relays are so arranged that their electric contacts form an integrating part of the magnetic circuit. Therefore, said magnetic circuit may not form a closed electric circuit. When using a core of cobalt ferrite an insulating separator has to be introduced in the magnetic circuit, which means an extra air gap that highly reduces the effectivity of the magnetic circuit.

The following requirements may be specified for a ferrite that is in all respects acceptable for pulse relay cores:

Volume resistivity  $\text{mohm cm.} \geq 20$   
Magnetostatic coercive force ( $H_c$ )  $\text{öersteds} \geq 20$   
Magnetostatic remanence value ( $B_r$ ), gauss  $\geq 2800$

Magnetostatic remanence ratio ( $B_r/B_m$ )  $\geq 0.75$   
Magnetostatic coercive force ratio  
( $H_m(k)/H_c(k)$ )  $\leq 1.7$   
Energy loss ratio ( $H_c(d)/H_c(st)$ )  $\leq 2$

5 Regarding the used letter symbols reference is made to the attached drawing in which FIG. 1 shows hysteresis loops for a ferrite material at magnetostatic magnetization as well as at dynamic magnetization and FIG. 2 shows the coercive force  $H_c$  as a function of the maximum magnetization field  $H_m$ . With magnetostatic magnetization is meant a magnetization at which the magnetization current is raised from 0-value to maximum value so slowly, that the least possible energy losses occur, and by dynamic magnetization is meant a magnetization with an instant raising of the current to maximum value. Thus  $H_c(d)$  is the coercive force at dynamic magnetization,  $H_c(st)$  the coercive force at magnetostatic magnetization, and  $H_m(k)$  the value of the magnetizing field at which an increase gives only an insignificant increase of the magnetic energy of the ferrite. The magnetostatic remanence ratio is defined as the ratio between the magnetostatic remanence  $B_r$  and the magnetization  $B_m$ . The magnetostatic coercive force ratio is defined as the ratio between the value of the magnetizing field force  $H_m(k)$  and the corresponding coercive force  $H_c(k)$ . The energy loss ratio finally is defined as the ratio between the coercive force at dynamic magnetizing  $H_c(d)$  and the coercive force at magnetostatic magnetizing  $H_c(st)$  and constitutes a good approximation for the ratio between required energy in the two magnetization cases. The amount of energy is represented by the size of the surface enclosed within the respective hysteresis loop (FIG. 1). The difference between the sizes of these surfaces represents the energy loss caused by the magnetic relaxation distortion at pulsing.

10 By the invention a ferrite is obtained that completely fulfils the requirements given above, and the invention is especially characterized partly by the oxide mixture being composed substantially according to the molecular formula  $Co_{1+x-y}Zn_yFe_{2-2x}O_{4-2x}$ , in which formula

$$0.01 \leq x \leq 0.04, y \geq \frac{1+x}{10}$$

15 and whereby up to 50% of Zn may be substituted by Cd and up to 5 atomic percent of Fe may be substituted by Mn and partly by said oxide mixture being exposed to a temperature shot comprising a rapid raise of about 100° C. in excess of the final sintering temperature at an arbitrary moment during said holding time of the final sintering temperature and immediately thereafter following reduction of temperature of the same.

20 The procedure is further explained in the following by means of two examples:

## 55 Example 1

Cobalt zinc ferrite according to the molecular formula  $Co_{0.83}Zn_{0.17}Fe_{1.94}O_{3.94}$  ( $x=0.03; y=0.20$ ).

25 A finely pulverized mixture of Grams

60 Black cobalt oxide ( $Co_2O_3$ )	294
Zinc oxide ( $ZnO$ )	70
Red iron oxide ( $Fe_2O_3$ )	664

30 is moistened and pressed to slabs. The slabs are sintered preliminarily by heating in air with a heating up speed of 100° C. per hour to 1000° C. After a holding time of 2 hours at 1000° C. the glowing slabs are cooled off in water and thereafter pulverized to a grain size of  $1\mu$ .

35 To one kilogram dry powder is added 120 ml. of a 25% polyvinyl alcohol solution in water. The material is well mixed, granulated, and dried to a moisture content of about 1%. Thereafter, a Zn-stearat powder is added at an

amount corresponding to 0.2% of the weight of the mixture, whereby the stearat powder has to be well worked into said mixture. This is thereafter moulded to form bodies at a pressure that gives a volume weight of about 3 g./cm.<sup>3</sup> of the moulded body.

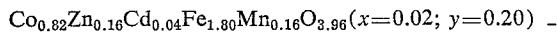
The bodies are thereafter sintered in a final sintering oven, the heating up being performed with a speed of 100° C. per hour to a temperature of 1150° C. After a four hour holding time at 1150° C. the sintering temperature is rapidly raised to 1250° C. whereafter the form bodies immediately are rapidly cooled off in air to a temperature below 200° C.

The ferrite material thus obtained has the following properties.

Volume weight	g./cm. <sup>3</sup>	4.7-5.2	15
Volume resistivity	mohm cm	59-65	
Magnetostatic coercive force	oersteds	38-40	
Magnetostatic remanence value	gauss	3400-3500	
Magnetostatic remanence ratio		0.79-0.80	10
Magnetostatic coercive force ratio		1.5	
Energy loss ratio		2	20

### Example 2

Cobalt zinc ferrite according to the molecular formula



A finely ground mixture of

	Grams	
Black cobalt oxide (Co <sub>2</sub> O <sub>3</sub> )	288	
Zinc oxide (ZnO)	55	25
Cadmium oxide (CdO)	22	
Red iron oxide (Fe <sub>2</sub> O <sub>3</sub> )	611	
Manganese carbonate (MnCO <sub>3</sub> )	79	

is sintered preliminarily by heating in air to 1000° C. with a holding time of 1 hour at this temperature. After cooling the sintering product is finely pulverized and dried. The dry ferrite powder is mixed with a convenient mould lubricant, granulated and pressed to cores.

At the final sintering process the cores are heated up at a heating speed of 100° C. per hour to a temperature of 1350° C., whereafter the cores are immediately cooled down to 1250° C. After a holding time of 3 hours at 1250° C. the cores are cooled in the oven to 950° C. at which temperature the oven is held during 18 hours. Thereafter the cores are rapidly cooled down to room temperature.

The cores thus obtained have the following properties:

Volume weight	g./cm. <sup>3</sup>	4.9-5.1	15
Volume resistivity	mohm cm	50-61	
Magnetostatic coercive force	oersteds	36-39	
Magnetostatic remanence value	gauss	3050-3150	
Magnetostatic remanence ratio		0.79	40
Magnetostatic coercive force ratio		1.6	
Energy loss ratio		2	45

In order to obtain a high remanence value it is necessary that the cores should be sintered to a specific volume weight of at least 4.8 and, therefore, the bodies should be held at a temperature between 1100° C. and 1300° C. during a time of 2-4 hours. The optimum seems to be a holding time of 3 hours at a temperature of 1150°-1250° C.

In order to obtain the desired Hc-value at the given high volume weight the cores are exposed to a temperature shot of about 100° C. above the high final sintering temperature and is because of practical reasons performed at the beginning or the end of the holding time. With respect to the effects of this temperature shot it is, however, of no importance at which time it is effectuated.

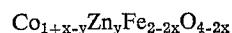
The final cooling off at the last sintering process should

generally be rapid as this gives a square hysteresis loop. It is often of advantage to carry out the cooling off in two stages by interrupting the cooling off at a temperature in the interval between 750° C.-1050° C. and maintaining the cores at this temperature during a time of 12-18 hours. By this procedure it is assured that the individual cores have, as far as possible, equal properties.

In order to obtain a high volume resistivity it is generally sufficient that the final sintering process is carried out in air, whereby the oxygen of the air sustain the oxidation of the metals. In order to further increase the volume resistivity and the volume weight it may sometimes be convenient to provide oxygen gas during the time the final sintering temperature is above 950° C.

We claim:

1. Process for manufacturing a ferrite material with high volume resistivity, relatively high coercive force, and high remanence value comprising preliminarily sintering a pulverized oxide mixture composed according to the following molecular formula:



in which formula

$$0.01 \leq x \leq 0.04, y \geq \frac{1+x}{10}$$

and wherein up to 50% of the amount of Zn may be substituted by Cd and up to 5 atomic percent of the amount of Fe may be substituted by Mn, the sintered product after cooling down being pulverized and moulded to convenient form bodies, exposing said bodies to a final sintering process including heating up to a predetermined final sintering temperature and maintaining said final sintering temperature constant during a predetermined holding time with the exception of a short interval during which the form bodies are exposed to a temperature shot comprising a rapid temperature rise of about 100° C. in excess of said final sintering temperature with an immediately thereafter following reduction of the temperature of equal magnitude, said temperature shot being effectuated at an arbitrary moment during said holding time.

2. Process according to claim 1 wherein the final cooling down of the form bodies is carried out rapidly.

3. Process according to claim 1, wherein the cooling down of the form bodies after the final sintering process is carried out in two stages with a duration of at least 10 hours at a temperature within the temperature interval 750° C.-1050° C.

4. Process according to claim 1 wherein the temperature shot is effectuated at the beginning of said holding time.

5. Process according to claim 1 wherein the temperature shot is effectuated at the end of said holding time.

6. Process according to claim 1 wherein said final sintering process is carried out in air.

7. Process according to claim 1 wherein oxygen gas is provided at the final sintering process during the time the temperature exceeds 950° C.

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