

# PATENT SPECIFICATION

DRAWINGS ATTACHED

L076.986

L076.986



Date of Application and filing Complete Specification: Aug. 27, 1964.

No. 35220/64.

Application made in United States of America (No. 305236) on Aug. 28, 1963.

(Patent of Addition to 989389 dated Dec. 20, 1962).

Complete Specification Published: July 26, 1967.

© Crown Copyright 1967.

Index at acceptance: —H1 H(2, 3C, 3F, 6B, 9)

Int. Cl.: —H 01 f 1/10

## COMPLETE SPECIFICATION

### Ferrite Core and Method of Manufacture thereof

We, RADIO CORPORATION OF AMERICA, a Corporation organized under the laws of the State of Delaware, United States of America, of 30, Rockefeller Plaza, City and State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a ferromagnetic ferrite core which exhibits a substantially square hysteresis loop, a relatively high Curie temperature, and a relatively low coercive force. More particularly, this invention relates to an improved method of manufacture of the magnetic core described and claimed in our Patent No. 989,389.

Our Patent No. 989,389 claims a magnetic core having a squareness ratio  $R_s$  of at least 0.70 comprising a ceramic of sintered particles having the molar composition:



where:

Me is at least one member of the group consisting of Cd, Zn, Mg and Mo.

w is between 0.00 to 0.15,

x is between 0.005 to 0.05 when Me is at least one of Cd, Zn and Mg and is 0.005 to 0.2 when Me is Mo, and

y is between 2.35 to 2.50.

Me may be at least Mo.

This magnetic core was made by various described methods which required the core to be sintered in a mixture of mostly inert gas.

We have found that the method of making the core can be improved by sintering the core in an atmosphere either consisting essentially of oxygen itself, or oxygen-neutral gas mixtures of high oxygen content.

Accordingly, the present invention provides a method of manufacturing a magnetic

core comprising the steps of calcining, in an oxidizing atmosphere, a mixture of oxides or oxide yielding compounds to provide a material having the formula:  $Li_{0.5} Mn_w Mo_z Me_y O_4$  where: Me is at least one of the groups Cd, Zn, Mg, w is between 0.00 to 0.015, z is between 0.005 to 0.02, v is between 0.000 to 0.05, and y is between 2.35 to 2.50; shaping a quantity of said calcined mixture to form a core; sintering said core at temperatures between 1050° and 1190°C for between 1 and 24 hours in an atmosphere consisting essentially of oxygen or of oxygen containing not more than 10% neutral gas; and then cooling said core.

The terms "core" and "body" are used interchangeably herein to refer to a sintered mass of ferrite particles.

#### EXAMPLE

A magnetic core was prepared in accordance with the present invention by the following method. Mix a batch of the following ingredients:

| Molar Parts | Ingredient                          |
|-------------|-------------------------------------|
| 0.5         | Li, as lithium carbonate $Li_2CO_3$ |
| 0.04        | Cd, as cadmium oxide $CdO$          |
| 0.01        | Mo, as molybdenum oxide $MoO_3$     |
| 2.47        | Fe, as ferric oxide, $Fe_2O_3$      |

The batch is attrited in ethyl alcohol for approximately 2 hours and then dried and screened. The attrited mixture is calcined for approximately 4 hours in air at approximately 900°C. The calcined batch is attrited in ethyl alcohol for approximately 2 hours and then dried. Approximately three per cent by weight of a suitable organic binder is evenly dispersed through the dry calcined batch. One suitable binder is Flexalyn in methyl ethyl ketone, which is marketed by the Hercules Powder Company,

[Price 4s. 6d.]

Wilmington, Delaware, United States of America.

The calcined batch with the binder added is screened through an 80 mesh screen. The screened calcined batch is then pressed into toroidal cores. The pressed cores are then sintered for approximately 8 hours at approximately 1125°C in an atmosphere of pure oxygen gas. The sintered cores are cooled at the rate of approximately 50°C per hour in an atmosphere of flowing oxygen to approximately 700°C, and then cooled to room temperature.

The range of molar composition of the core is:  $\text{Li}_{0.5} \text{Mn}_x \text{Me}_x \text{MO}_3 \text{Fe}_y \text{O}_z$ , where Me is at least one member of the group consisting of Cd, Zn, and Mg. Me may consist of any combination of members of this group. The value of x may be between 0.00 and 0.05. The value of w may be between 0.00 and 0.15. The value of y may be between 2.35 and 2.60. The value of z may be between 0.005 and 0.02.

In the EXAMPLE, the steps of mixing, attriting, drying, and screening are designated to provide an intimate mixture of the ingredients, and to remove gases, water, and volatile organic matter contained in the batch. These steps are not critical. Any procedure which provides a dry, intimate mixture of the ingredients is satisfactory.

The calcining temperature is between 800° and 1000°C, and is preferably near the middle of the range. The calcining time is not critical, although shorter times are preferred with higher calcining temperatures. Air is the preferred calcining atmosphere. Other atmospheres having oxidizing characteristics similar to that of air at the calcining temperature may also be used.

The sintering temperature is between 1050° and 1190°C. The sintering temperature affects the coercivity of the core and the grain size of the crystallites which constitute the core. Generally, the higher the sintering temperature, the lower the coercivity of the core and the larger the grain size of the crystallites. Using the method of the EXAMPLE, cores can be made having a coercivity between 2.0 and 2.4 oersteds by selecting the sintering temperature between 1050° and 1190°C.

The sintering time is between 1 and 24 hours. The sintering time also affects the coercivity of the cores. Generally, the longer the sintering time, the lower the coercivity of the core. Using the method of the EXAMPLE, cores can be made having a coercivity between 1.7 and 2.6 oersteds

by selecting the sintering time between 1 and 16 hours.

Annealing may take place during cooling at temperatures between 700° and 1100°C. The annealing time is between 1 and 10 hours. The cooling rate of the core down to 700°C affects the squareness ratio of the core. Generally, the faster the cooling rate, the lower the squareness ratio  $R_s$ . Using the method of the EXAMPLE, cores can be made having a squareness ratio  $R_s$  between 0.90 and 0.72, by selecting the cooling rate between 50°C per hour and quenching.

The sintering atmosphere is important. The cores are sintered in an atmosphere consisting essentially of oxygen gas or a mixture of a neutral gas and oxygen gas. The sintering atmosphere contains the volume ratio of neutral gas to oxygen gas is between a ratio of 0/1 and a ratio of 9/1. The cores are annealed in an atmosphere consisting essentially of a mixture of a neutral gas and oxygen gas or of oxygen gas alone. In the annealing atmosphere, the volume ratio of neutral gas to oxygen is between a ratio of 0/1 and a ratio of 6/1. Some suitable neutral gases for both the sintering step and the annealing step are nitrogen, argon, neon, helium, and mixtures thereof.

Alternative to carrying out the sintering and annealing steps in one firing operation as described above, the cores described herein may be prepared by sintering in an atmosphere as described above, cooling to room temperature, then refiring in an atmosphere as described above to anneal the cores, and finally cooling again to room temperature. Magnetic cores with similar characteristics to the core of the EXAMPLE are produced by this two-fire process.

Where cores are prepared by the two-fire process, the annealing or refiring temperature affects the squareness ratio  $R_s$ , and the switching time,  $T_s$ , of the core. Generally, the higher the annealing temperature, the higher the squareness ratio,  $R_s$ , and the longer the switching time. For example, by adding a refiring step to the method of the EXAMPLE, it was found that raising the annealing temperature from 800°C to 1100°C, raises the squareness ratio from approximately 0.89 to approximately 0.92 and changes the switching time,  $T_s$ , from approximately 0.79 microseconds to 0.90 microseconds.

The following TABLE tabulates additional examples of cores prepared by the method of the EXAMPLE but differing in at least one of sintering time, sintering temperature, and cooling rate.

TABLE  
 $\text{Li}_{0.5}\text{Cd}_{0.04}\text{Mo}_{0.01}\text{Fe}_{2.47}\text{O}_4$

|    | Sintering<br>Temperature | Sintering<br>Time-hours | Cooling<br>Rate | Hc     | Rs   |
|----|--------------------------|-------------------------|-----------------|--------|------|
| 5  | 1125°C                   | 4                       | 50°C/hr         | 2.1 oe | 0.92 |
|    | 1125                     | 8                       | 50              | 2.0    | 0.88 |
|    | 1125                     | 16                      | 50              | 1.7    | 0.92 |
|    | 1150                     | 8                       | 50              | 2.2    | 0.89 |
| 10 | 1150                     | 8                       | 100             | 2.2    | 0.88 |
|    | 1150                     | 8                       | 200             | 2.2    | 0.83 |
|    | 1150                     | 8                       | Quench          | 2.1    | 0.71 |

WHAT WE CLAIM IS:—

1. A method of manufacturing a magnetic core comprising the steps of calcining, in an oxidizing atmosphere, a mixture of oxides or oxide yielding compounds to provide a material having the formula:  $\text{Li}_{0.5}\text{Mn}_w\text{Mo}_z\text{Me}_y\text{Fe}_v\text{O}_4$  where: Me is at least one of the group  $\text{Ca}$ ,  $\text{Zn}$ ,  $\text{Mg}$ , w is between 0.00 to 0.15, z is between 0.005 to 0.02, v is between 0.000 to 0.05, and y is between 2.35 to 2.50; shaping a quantity of said calcined mixture to form a core; sintering said core at temperatures between 1050° and 1190°C for between 1 and 24 hours in an atmosphere consisting essentially of oxygen or of oxygen containing not more than 10% neutral gas; and then cooling said core.
2. A method according to Claim 1 wherein the calcining step is carried out at a temperature of between 800° and 1000°C.

3. A method according to Claim 1 or Claim 2 wherein the core is cooled at a rate of between 50°C per hour and quenching.

4. A method of manufacturing a magnetic core substantially as hereinbefore described in the EXAMPLE.

5. A method according to any one of the preceding Claims and comprising the additional steps of refiring the cooled core in an atmosphere substantially identical to said sintering atmosphere, so as to anneal the core, and finally cooling said core.

6. A method according to any preceding Claim wherein annealing of the core takes place at temperatures between 700° and 1100°C.

A. & Wm CLARK,  
 Chartered Patent Agents,  
 5 Stone Buildings, Lincoln's Inn,  
 London, W.C.2.

TABLE  
 $\text{Li}_{0.5}\text{Cd}_{0.04}\text{Mo}_{0.01}\text{Fe}_{2.47}\text{O}_4$

|    | Sintering<br>Temperature | Sintering<br>Time-hours | Cooling<br>Rate | Hc     | Rs   |
|----|--------------------------|-------------------------|-----------------|--------|------|
| 5  | 1125°C                   | 4                       | 50°C/hr         | 2.1 oe | 0.92 |
|    | 1125                     | 8                       | 50              | 2.0    | 0.88 |
|    | 1125                     | 16                      | 50              | 1.7    | 0.92 |
|    | 1150                     | 8                       | 50              | 2.2    | 0.89 |
|    | 1150                     | 8                       | 100             | 2.2    | 0.88 |
| 10 | 1150                     | 8                       | 200             | 2.2    | 0.83 |
|    | 1150                     | 8                       | Quench          | 2.1    | 0.71 |

WHAT WE CLAIM IS:—

1. A method of manufacturing a magnetic core comprising the steps of calcining, in an oxidizing atmosphere, a mixture of oxides or oxide yielding compounds to provide a material having the formula:  $\text{Li}_{0.5}\text{Mn}_w\text{Mo}_z\text{Me}_v\text{Fe}_y\text{O}_4$  where: Me is at least one of the group  $\text{Ca}$ ,  $\text{Zn}$ ,  $\text{Mg}$ ,  $w$  is between 0.00 to 0.15,  $z$  is between 0.005 to 0.02,  $v$  is between 0.000 to 0.05, and  $y$  is between 2.35 to 2.50; shaping a quantity of said calcined mixture to form a core; sintering said core at temperatures between 1050° and 1190°C for between 1 and 24 hours in an atmosphere consisting essentially of oxygen or of oxygen containing not more than 10% neutral gas; and then cooling said core.

2. A method according to Claim 1 wherein the calcining step is carried out at a temperature of between 800° and 1000°C.

3. A method according to Claim 1 or Claim 2 wherein the core is cooled at a rate of between 50°C per hour and quenching.

4. A method of manufacturing a magnetic core substantially as hereinbefore described in the EXAMPLE.

5. A method according to any one of the preceding Claims and comprising the additional steps of refining the cooled core in an atmosphere substantially identical to said sintering atmosphere, so as to anneal the core, and finally cooling said core.

6. A method according to any preceding Claim wherein annealing of the core takes place at temperatures between 700° and 1100°C.

A. & Wm CLARK,  
 Chartered Patent Agents,  
 5 Stone Buildings, Lincoln's Inn,  
 London, W.C.2.

