(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 337 716 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication of patent specification : **01.03.95 Bulletin 95/09**

(51) Int. Cl.[6] : **H01F 1/18**, H01F 27/24, H01F 41/02

(21) Application number : **89303542.8**

(22) Date of filing : **11.04.89**

(54) **Magnetic ribbon and magnetic core.**

(30) Priority : **11.04.88 JP 88694/88**

(43) Date of publication of application : **18.10.89 Bulletin 89/42**

(45) Publication of the grant of the patent : **01.03.95 Bulletin 95/09**

(84) Designated Contracting States : **AT BE CH DE ES FR GB GR IT LI LU NL SE**

(56) References cited :
EP-A- 0 214 305
PATENT ABSTRACTS OF JAPAN, vol. 11, no. 185 (C-428)[2632], 13th June 1987; & JP-A-62 10 278 (KAWASAKI STEEL CORP.) 19-01-1987
PATENT ABSTRACTS OF JAPAN, vol. 10, no. 145 (E-407)[2202], 28th May 1986; & JP-A-61 8903 (KAWASAKI SEITETSU K.K.) 16-01-1986
PATENT ABSTRACTS OF JAPAN, vol. 12, no. 30 (E-578)[2877], 28th January 1988; & JP-A-62 188 209 (TDK CORP.) 17-08-1987
PATENT ABSTRACTS OF JAPAN, vol. 11, no. 249 (E-532)[2696], 13th August 1987; & JP-A-62 61 308 (TOSHIBA CORP.) 18-03-1987

(73) Proprietor : **MITSUI PETROCHEMICAL INDUSTRIES, LTD.**
2-5, Kasumigaseki 3-chome
Chiyoda-ku
Tokyo 100 (JP)

(72) Inventor : **Matsuoka, Takashi**
c/o Mitsui Petrochem. Ind. Ltd.
3, Chigusa Kaigan
Ichihara-shi Chiba-ken (JP)
Inventor : **Furihata, Toshikazu**
c/o Mitsui Petrochem. Ind. Ltd.
3, Chigusa Kaigan
Ichihara-shi Chiba-ken (JP)
Inventor : **Ueda, Yasushi**
c/o Mitsui Petrochem. Ind. Ltd.
3, Chigusa Kaigan
Ichihara-shi Chiba-ken (JP)

(74) Representative : **Senior, Alan Murray et al**
J.A. KEMP & CO.,
14 South Square,
Gray's Inn
London WC1R 5LX (GB)

EP 0 337 716 B1

Description

The present invention relates to a magnetic ribbon and a magnetic core formed by using said magnetic ribbon.

If a magnetic core is formed by winding or laminating a magnetic ribbon, and if insulation between layers of the ribbon is poor, an eddy current flowing across the ribbon layers occurs and an increase in eddy current losses results in an increase in overall core losses (magnetic losses). This tendency is particularly noticeable in the case of high frequencies. In addition, the frequency characteristics of permeability is poor, and it is impossible to expect any advantageous use at 100 kHz or more.

Accordingly, in order to improve insulation between ribbon layers, an insulating layer formed of a nonmagnetic material is conventionally provided between the ribbon layers, and a uniform insulating film is formed on the ribbon surface as one means thereof, so as to solve the aforementioned problem.

In cases where an amorphous magnetic ribbon is processed as a magnetic ribbon, annealing is usually carried out at 400°C or thereabouts. However, if such annealing is carried out, because of a difference in the coefficient of linear expansion, i.e., since the coefficient of linear expansion of the insulating film is greater than that of the amorphous ribbon, compressive stress occurs in the ribbon, and magnetic characteristics deteriorate due to the adverse effect of magnetostriction.

In addition, there is another problem in that materials of such insulating films capable of withstanding annealing at 400°C or thereabouts are limited. Furthermore, if a magnetic core is formed by providing an insulating film, the filling factor (space factor) declines, which disadvantageously causes the magnetic core to become large in size.

Thus, as described above, when producing a magnetic core by using a magnetic ribbon, an insulating film is generally interposed between ribbon layers, and the greatest matter of concern to those skilled in the art lies in finding an insulating material having an excellent insulating performance.

JP-A-62/10278 describes an alloy strip coated with colloidal silica in a metallic phosphate solution and upon this document, the prior art portion of claims 1 and 4 are based.

EP-A-0 214 305 describes an alloy strip coated with an adhesive of a borosilicone resin for producing a laminated core.

In accordance with the present invention, there is provided a magnetic ribbon for winding or lamination into a magnetic core, the magnetic ribbon being formed of an amorphous metal and having fine particles coated on at least one surface thereof said fine particles having electrically-insulating properties;

characterised in that said fine particles are antimony pentoxide particles having a size in the range of from 10 nm to 2 μm, and in that the fine particles are coated on said at least one surface in an amount in the range of from 10^{-7} cm^3 to 2×10^{-4} cm^3 per cm^2 of surface area.

The invention also provides a process for making the ribbon and a magnetic core of such a ribbon wound therearound or laminated thereon.

The particles may be attached so as to secure a layer of air so that in the absence of a conventional insulating film, the air present between the layers can serve as an insulating layer and prevent an eddy current, and the space factor can be made as large as possible.

That is,particles formed of antimony pentoxide are attached on at least one surface of the magnetic ribbon, so that if the magnetic ribbon is wound or laminated to form a magnetic core, the particles serve as a spacer, thereby forming a layer of air between adjacent layers of the ribbon.

However, the particles may be attached uniformly and densely on at least one surface of the ribbon. In this case, rather than particularly securing a layer of air, the particles themselves function as an insulating layer. Nevertheless, in this case as well, it is possible to obtain the same effect as that obtained by securing a layer of air by means of the particles. Accordingly, the present invention includes both the case where the particles are attached coarsely and the case where they are attached densely.

The particles may be applied by any suitable method for example by passing the magnetic ribbon through a suspension containing the particles. Where it is intended that the particles should act as a spacer trapping a layer of air between layers or windings of a core the proportion of particles in the suspension may be chosen to be suitably low. For example, when suspended in toluene, they may form 1% to 10%, preferably 2% to 5%, e.g. about 3%, by weight of the suspension.

Where it is intended that the particles should be attached more densely so as to act as the insulation then a higher proportion may be used in the suspension. For example, with the same materials as above, above 20% by weight, for example 20% to 50%, e.g. about 30% by weight.

Thus with the present invention a magnetic ribbon and a magnetic core can be provided having excellent magnetic characteristics while securing insulating properties between ribbon layers with the space factor reduced.

The invention will be further described by way of non-limitative example with reference to the accompanying drawings, in which :-

Figs. 1 to 3 are graphs illustrating magnetic characteristics in accordance with a first embodiment of the present invention, in which

Fig. 1 illustrates B-H characteristics;

Fig. 2 illustrates the frequency characteristics of core loss; and

Fig. 3 illustrates the frequency characteristics of permeability;

Figs. 4 to 6 are graphs illustrating the magnetic characteristics in accordance with a second embodiment of the present invention, in which

Fig. 4 illustrates B-H characteristics;

Fig. 5 illustrates the frequency characteristics of core loss; and

Fig. 6 illustrates the frequency characteristics of permeability; and

Fig. 7 illustrates the outline of apparatus for attaching fine particles; and

Fig. 8 is a diagram schematically illustrating means for producing a toroidal type magnetic core.

Referring now to the accompanying drawings, a description will be given of the preferred embodiments of the present invention.

The magnetic ribbon referred to in the present invention is a thin magnetic strip, and, as magnetic materials, it is possible to cite the following: ferromagnetic elements such as Fe, Co, and Ni among transition metals, alloys of ferromagnetic elements, alloys of ferromagnetic elements and nonferromagnetic elements which are added to improve characteristics, ferrite, permalloy, amorphous alloys, etc. As amorphous alloys, it is possible to cite Fe-based alloys such as Fe-B, Fe-B-C, Fe-B-Si, Fe-B-Si-C, Fe-B-Si-Cr, Fe-Co-B-Si, and Fe-Ni-Mo-B, Co-based alloys such as Co-B, Co-Fe-Si-B, Co-Fe-Ni-Mo-B-Si, Co-Fe-Ni-B-Si, Co-Fe-Mn-B-Si, Co-Fe-Mn-Ni, Co-Mn-Ni-B-Si, and Co-Fe-Mn-Ni-B, and other similar alloys.

Inorganic fine particles of antimony pentoxide are attached to such a magnetic ribbon. Antimony pentoxide is non-magnetic, and has insulating properties. If the fine particles are magnetic and conductive, an averse effect is exerted on magnetic characteristics, and an eddy current is liable to flow.

As for the size of the fine particles of the inorganic substance, if consideration is paid to the fact that the fine particles are attached to the ribbon uniformly so as to form an insulating layer, the size of the fine particles may be small. However, if the particle size is made too small, it constitutes a factor making manufacture difficult. Meanwhile, if the particle size is too large, when the magnetic core is formed by a ribbon, the gap between the adjacent layers of the ribbon becomes too large, so that the space factor of the magnetic material becomes small. For this reason, it is preferred that the size of the fine particles is set in the range of 10 nm to 2 μm.

In addition, as for the amount of the fine particles attached, the fine particles may preferably be attached in such a manner that they are attached by 10^{-7} cm^3 to 2×10^{-4} cm^3, more preferably 3×10^{-6} cm^3 to 10^{-5} cm, per unit area (1 cm^2). If this amount attached is calculated into the weight of fine particles per unit area, it is 3.8×10^{-7} g/cm^2 to 7.6×10^{-4} g/cm^2, preferably 1.1×10^{-5} g/cm^2 to 3.8×10^{-5} g/cm^2.

Means for attaching the fine particles is so arranged that these fine particles are dispersed in water or a volatile organic solvent such as toluene and, after this solution is applied to the ribbon surface, force or natural drying is carried out, thereby allowing the fine particles to be attached to the ribbon. The concentration of this solution determines the amount of fine particles to be attached to the ribbon. In other words, the antimony pentoxide may be dispersed in toluene in a colloidal state at a rate of from 0.1 to 30 wt% with respect to toluene. 3 wt% or thereabouts in this range is also effective, a decline in the space factor is practically nil, and the magnetic characteristics do not deteriorate. The thickness of the film of the solution applied is preferably 10 μm or less in determining the aforementioned amount of fine particles to be attached. In addition, a drying furnace may be used for evaporation of the solvent depending on the solvent, and drying may be carried out at 100°C or above.

With respect to the magnetic ribbon, or an amorphous ribbon, in particular, annealing may be carried out for 0.5 to 5 hours at a temperature of 300°C to 500°C in an inert gas atmosphere such as nitrogen so as to eliminate strain, as required. This annealing may be effected after the ribbon is wound or laminated into a magnetic core, or may be effected in the state of the ribbon. In particular, when annealing is effected at a temperature 10 to 50°C higher than the Curie point, a magnetic core exhibiting excellent characteristics with respect to high frequencies can be obtained. Incidentally, annealing may be effected in a magnetic field or in a nonmagnetic field.

In addition, when the amorphous magnetic core with the ribbon wound therearound or laminated thereon is annealed since the fine particles disposed between adjacent ribbon layers are powders, the magnetic core is not subjected to linear expansion. The fine particles rather exhibit the action of absorbing the stress accompanying the shrinkage of the amorphous ribbon.

On the basis of the foregoing, a description will now be given of a method of producing a magnetic core in accordance with the present invention.

First, a magnetic ribbon and a solution containing fine particles are prepared. The solution containing the fine particles is applied to at lest one surface of the magnetic ribbon by any of the various methods of application, and the solvent is allowed to dry. The resultant magnetic ribbon with the fine particles attached thereto is wound under tension, thereby obtaining a toroidal-type magnetic core. Finally, annealing for eliminating strain is carried out, as necessary. Incidentally, tension applied at the time of winding is preferably 0.05 o 2 kg.

Meanwhile, when a laminated type magnetic core is produced, the ribbon with fine particles attached thereto is cut into a predetermined configuration, and the cut pieces are laminated so as to form the magnetic core. Annealing which is carried out as necessary may be effected prior to the lamination or after the magnetic core has been formed subsequent to the lamination.

Examples of the present invention will be described hereafter.

By using the apparatus shown in Fig. 7, an amorphous ribbon 1a (2605S-2, Fe_{78}-B_{13}-Si_9, 10 mm width) made by Allied Corp. is fed forward into a colloidal solution 2 of antimony pentoxide. When the amorphous ribbon 1a is lifted up, the amorphous ribbon 1a is clamped by a pair of bar coaters 3 so as to allow excess solution to drop. Then, while the ribbon 1a is being dried with hot air by means of a hot air drier 4, the ribbon 1a was taken up. As for the colloidal solution 2 of antimony pentoxide, toluene was used as the solvent, and 3 wt% of antimony was dispersed with respect to toluene 97 wt%.

Subsequently, as shown in Fig. 8, the ribbon 1b with the particles attached thereto was fed forward via a roller 5, and was wound under tension in a final stage, thereby forming an amorphous magnetic core 6. A plurality of magnetic cores having the same dimensions were then formed, and were subjected to annealing for two hours at 435°C in a nitrogen atmosphere.

With respect to the magnetic cores thus obtained, measurements were made of the B-H characteristics, frequency characteristics of the core loss, and frequency characteristics of permeability. As for the B-H characteristics, measurements were made of two cases: one in which a magnetic field of $10^4/4\pi$ A/m (10 Oe), and the other in which a magnetic field of $10^3/4\pi$ A/m (1 Oe) were applied.

In addition, a colloidal solution in which 30 wt% of antimony pentoxide was dispersed with respect to 70 wt% of toluene was applied to the ribbon 1a, and measurements were similarly made. The detailed conditions in the respective examples were as follows:

(1) Example 1 (3 wt% solution)

(a) Magnetic core: a toroidal core with the aforementioned ribbon wound therearound
Inside diameter: 23.00 mm
Outside diameter: 37.00 mm
Height: 10.00 mm
Mass: 42.00 kg
Density of the material: 7.18 g/m^3
Volume: 5.850×10^{-6} (m^3)
Effective sectional area: 6.207×10^{-5} (m^2)
Mean magnetic path length: 9.425×10^{-2} (m)
Space factor: 88.67% (ratio of the volume of the ribbon to the total volume)
Tension during magnetic ribbon winding: 0.8 kg

(b) Colloidal solution applied
Organic solvent: toluene, 100 wt%
Fine particles: antimony pentoxide, 3 wt%

(c) Results
* B-H characteristics are shown in Fig. 1.
* Frequency characteristics of core loss are shown in Fig. 2.
The number of turns of the primary winding around the core was 5, while the number of turns of the secondary winding was 10.
* Frequency characteristics of permeability are shown in Fig. 3.

The number of turns of the primary winding around the core was 10.
Measured magnetic field: $50/4\pi$ A/m (5 mOe)
Measured current: 2.65173 mA

(2) Example 2 (30wt% solution)

(a) Magnetic core: a toroidal core with the aforementioned ribbon wound therearound
Inside diameter: 23.00 mm
Outside diameter: 37.00 mm
Height: 10.00 mm
Mass: 25.57 g
Density of the material 7.18 g/m^3
Volume: 3.561×10^{-6} (m^3)
Effective sectional area: 3.779×10^{-5} (m^2)
Mean magnetic path length: 9.425×10^{-2} (m)
Space factor: 53.98%
Tension during the magnetic ribbon winding: 0.8kg

(b) Colloidal solution applied
Organic solvent: toluene, 70 wt%
Fine particles: antimony pentoxide, 30 wt%

(c) Results
* B-H characteristics are shown in Fig. 4.
* Frequency characteristics of core loss are shown in Fig. 5.
The number of turns of the primary winding around the core was 5, while the number of turns of the secondary winding was 10.
* Frequency characteristics of permeability are shown in Fig. 6.

The number of turns of the primary winding around the core was 10.
Measured magnetic field: $50/4\pi$ A/m (5 mOe)
Measured current: 2.65173 mA

From the foregoing results, it can be appreciated that the magnetic cores of the Examples display a hysteresis which is closer to a linear configuration, and that the core loss is low as a whole, and a rise in the high-frequency component can be reduced to a low level. A substantially fixed permeability was obtained up to 200 kHz.

As described above, in accordance with the present invention, since the above-described arrangement is adopted, it is possible to improve the magnetic characteristics at a frequency higher than 10 kHz, and the space factor can be made as large as possible, thereby making contributions to making the magnetic core compact.

Claims

1. A magnetic ribbon (1b) for winding or lamination into a magnetic core (6), the magnetic ribbon (1b) being formed of an amorphous metal and having fine particles coated on at least one surface thereof said fine particles having electrically-insulating properties;

   characterised in that said fine particles are antimony pentoxide particles having a size in the range of from 10 nm to 2 μm, and in that the fine particles are coated on said at least one surface in an amount in the range of from 10^{-7} cm^3 to 2 x 10^{-4} cm^3 per cm^2 of surface area.

2. A magnetic core (6) formed by winding or laminating a magnetic ribbon (1b) according to claim 1, wherein a layer of the fine particles is positioned between the adjacent magnetic ribbon layers and air is present between said adjacent magnetic ribbon layers together with said fine particle layer.

3. A process for manufacturing a metal core (6) comprising the steps of:

   a) winding or laminating the magnetic ribbon (1b) of claim 1; and
   b) annealing the wound or laminated magnetic ribbon for from 0.5 to 5 hours at a temperature in the range of from 300 to 500°C in an inert gas atmosphere.

4. A process for manufacturing a magnetic ribbon (1b) comprising the steps of:

   a) coating a dispersion (2) containing fine particles having electrically insulating properties on at least one surface of an amorphous metal ribbon (1a); and
   b) drying the coated ribbon (1a); characterised by:

   the further step of c) annealing the dried coated ribbon for from 0.5 to 5 hours at a temperature in the range of from 300 to 500°C in an inert gas atmosphere; and

   said fine particles being antimony pentoxide particles with a size in the range of from 10 nm to 2 μm and being attached to the surface in an amount in the range of from 10^{-7} cm^3 to 2 x 10^{-4} cm^3 per cm^2 of surface area.

5. A process for manufacturing a magnetic core, comprising the steps of:

   a) manufacturing a magnetic ribbon (1b) according to the process of claim 4; and
   b) winding or laminating the magnetic ribbon (1b) prior to said annealing step.

6. An electrical or electronic device comprising a magnetic core (6) according to claim 2.

Patentansprüche

1. Ein magnetisches Band (1b) zum Aufwickeln oder Anbringen in einem magnetischen Kern (6), wobei das magnetische Band (1b) aus einem amorphen Metall gebildet ist und mit feinen Partikeln auf wenigstens einer Oberfläche beschichtet ist, wobei die feinen Partikel elektrisch isolierende Eigenschaften haben; dadurch gekennzeichnet, daß die feinen Partikel Antimonpentoxid-Partikel sind, die eine Größe im Bereich von 10 nm bis 2 μm haben, und daß die feinen Partikel auf der wenigstens einen Oberfläche in einer Menge von $10^{-7}cm^3$ bis 2 x 10^{-4} cm^3 pro cm^2 Oberflächenbereich aufgebracht sind.

2. Eine magnetischer Kern (6) hergestellt durch Aufwickeln oder Anbringen eines magnetischen Bandes (1b) nach Anspruch 1, wobei eine Schicht der feinen Partikel zwischen den aneinander angrenzenden magnetischen Bandlagen angeordnet ist und Luft zwischen den aneinander angrenzenden magnetischen Bandlagen zusammen mit der feinen Partikelschicht vorhanden ist.

3. Ein Verfahren zur Herstellung eines metallischen Kerns (6) mit den Schritten:

   a) Aufwickeln oder Anbringen des magnetischen Bandes (lb) von Anspruch 1; und
   b) Tempern des gewickelten oder beschichteten magnetischen Bandes für zwischen 0,5 und 5 Stunden bei einer Temperatur im Bereich von 300 bis 500°C in einer Inertgasatmosphäre.

4. Ein Verfahren zur Herstellung eines magnetischen Bandes (1b) mit den Schritten:

   a) Beschichten einer Dispersion (2), die feine Partikel mit elektrisch isolierenden Eigenschaften auf wenigstens eine Oberfläche eines amorphen Metallbandes (1a); und
   b) Trocknen des beschichteten Bandes (1a); gekennzeichnet durch:
   den weiteren Schritt c) Tempern des getrockneten beschichteten Bandes für 0,5 bis 5 Stunden bei einer Temperatur im Bereich von 300 bis 500°C in einer Inertgasatmosphäre; und
   (das Merkmal, daß) die feinen Partikel Anti-

monpentoxid-Partikel mit einer Größe im Bereich von 10 nm bis 2 µm sind und an der Oberfläche in einer Menge in dem Bereich von 10^{-7} cm^3 bis 2 x 10^{-4} cm^3 pro cm^2 Oberflächenbereich aufgebracht sind.

5. Ein Verfahren zur Herstellung eines magnetischen Kerns, mit den Schritten:

a) Herstellen eines magnetischen Bandes (1b) gemäß dem Verfahren nach Anspruch 4; und

b) Aufwickeln oder Laminieren des magnetischen Bandes (1b) vor dem Temper-Schritt.

6. Eine elektrisches oder elektronisches Bauteil mit einem magnetischen Kern (6) nach Anspruch 2.

Revendications

1. Ruban magnétique (1b) destiné à être enroulé ou stratifié pour former un noyau magnétique (6), le ruban magnétique (1b) étant fait d'un métal amorphe et une de ses surfaces au moins étant recouverte de fines particules, lesdites fines particules ayant des propriétés d'isolation électrique, caractérisé en ce que lesdites fines particules sont des particules de pentoxyde d'antimoine ayant une taille comprise dans la fourchette de 10 nm à 2µm, et en ce que les fines particules sont déposées sur ladite surface au nombre d'au moins une en une quantité comprise entre 10^{-7} cm^3 et 2 x 10^{-4} cm^3 par cm^2 de superficie.

2. Noyau magnétique (6) formé par enroulement ou stratification d'un ruban magnétique (1b) conforme à la revendication 1, dans lequel une couche des fines particules est placée entre les couches adjacentes de ruban magnétique et de l'air est présent entre lesdites couches adjacentes de ruban magnétique en même temps que ladite couche de fines particules.

3. Procédé de fabrication d'un noyau métallique (6) qui comprend les étapes consistant à :

a) enrouler ou stratifier le ruban magnétique (1b) de la revendication 1, et

b) faire recuire le ruban enroulé ou stratifié pour une durée d'entre 0,5 et 5 heures, à une température comprise entre 300 et 500°C et dans une atmosphère de gaz inerte.

4. Procédé de fabrication d'un ruban magnétique (1b) qui comprend les étapes consistant à :

a) déposer une dispersion (2), qui contient de fines particules ayant des propriétés d'isolation électrique, sur une surface au moins d'un ruban (1a) en métal amorphe, et

b) sécher le ruban recouvert (1a), caractérisé par:

- l'étape supplémentaire (c) consistant à faire recuire le ruban recouvert séché pour une durée d'entre 0,5 et 5 heures, à une température comprise entre 300 et 500°C et dans une atmosphère de gaz inerte, et
- le fait que lesdites fines particules sont des particules de pentoxyde d'antimoine ayant une taille comprise dans la fourchette de 10 nm à 2µm, et sont déposées sur ladite surface au nombre d'au moins une en une quantité comprise entre 10^{-7} cm^3 et 2 x 10^{-4} cm^3 par cm^2 de superficie.

5. Procédé de fabrication d'un noyau magnétique qui comprend les étapes consistant à :

a) fabriquer un ruban magnétique (1b) selon le procédé de la revendication 4, et

b) enrouler ou stratifier le ruban magnétique (1b) avant ladite étape de recuit.

6. Dispositif électrique ou électronique qui contient un noyau magnétique (6) conforme à la revendication 2.

FIG.1

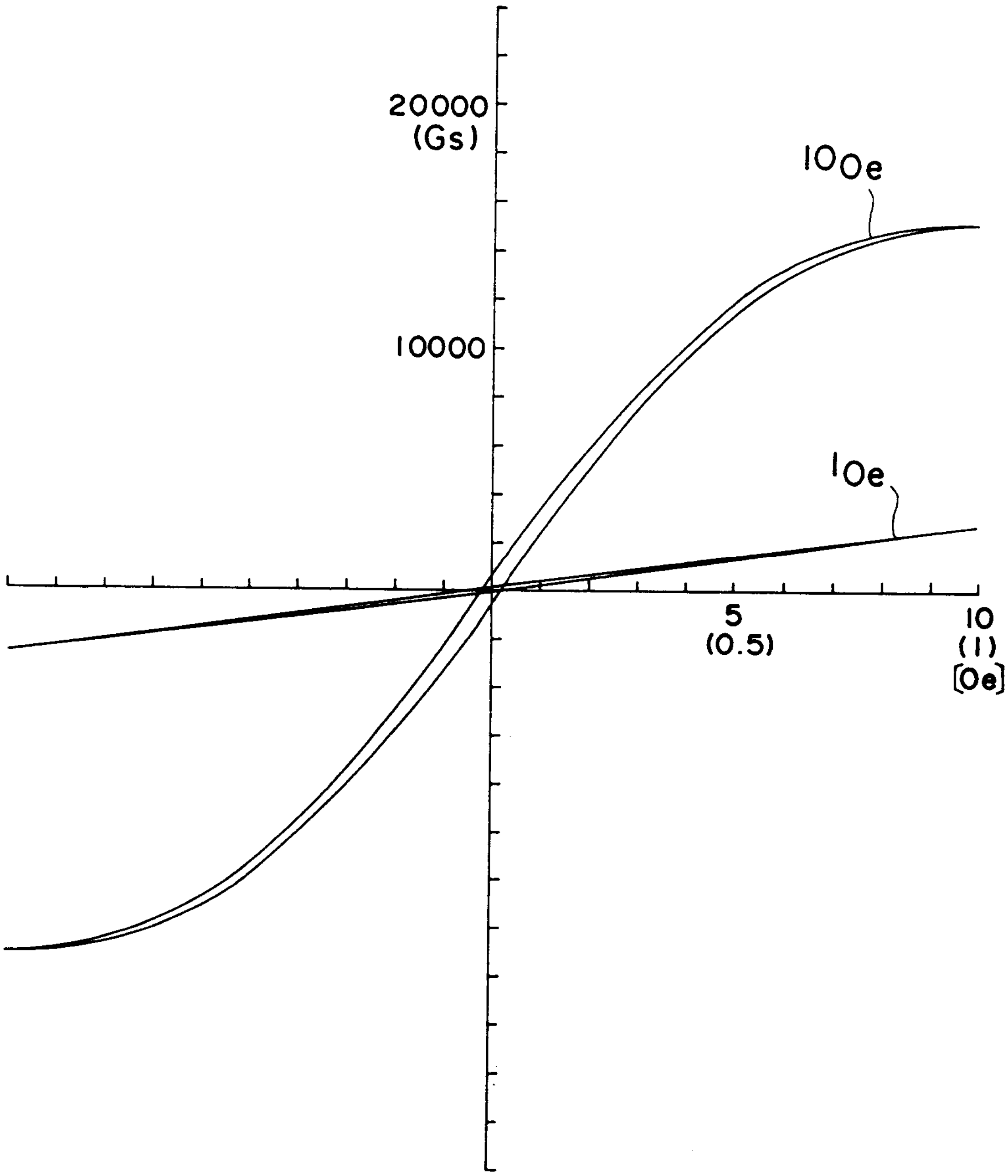

FIG.2

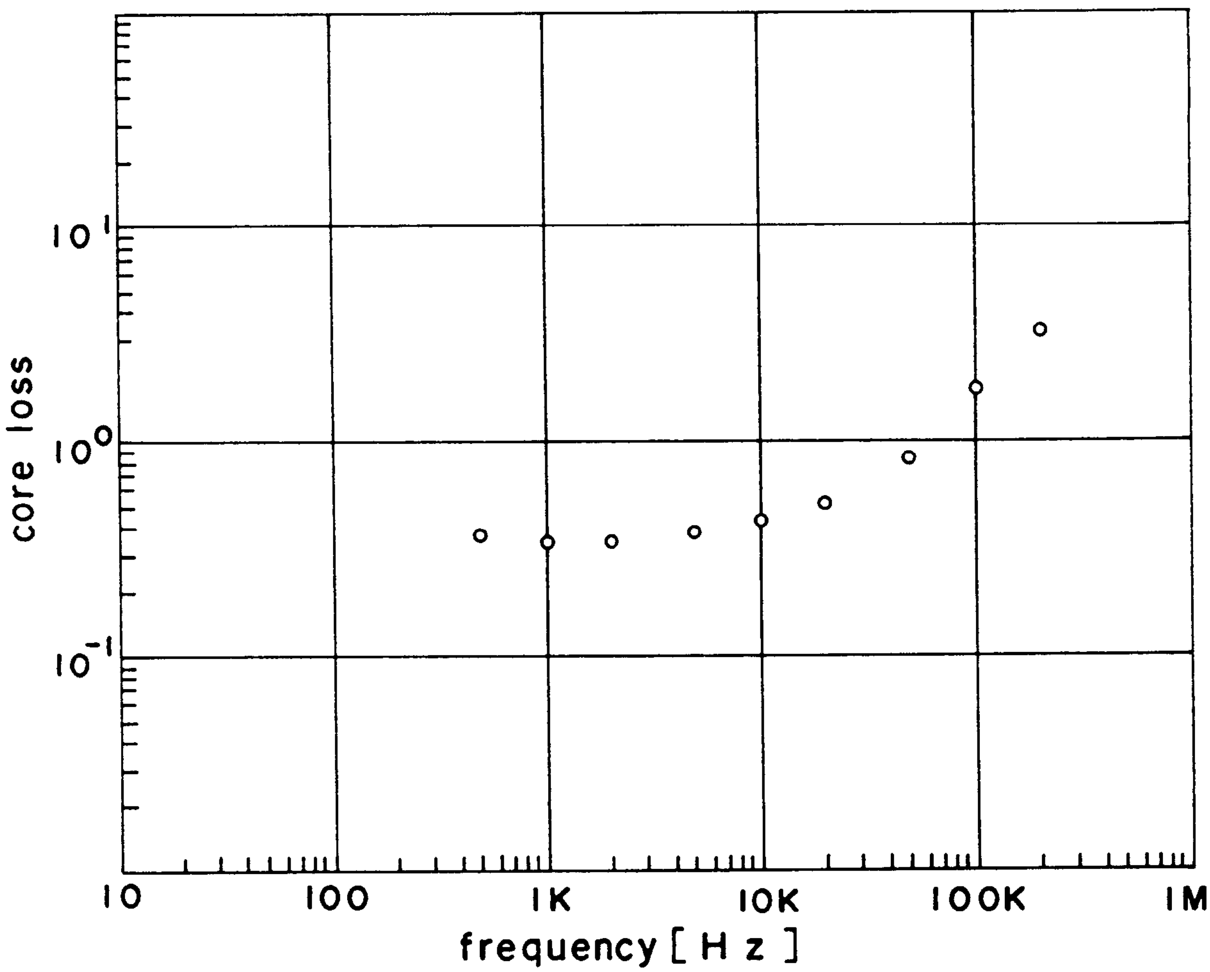

FIG.3

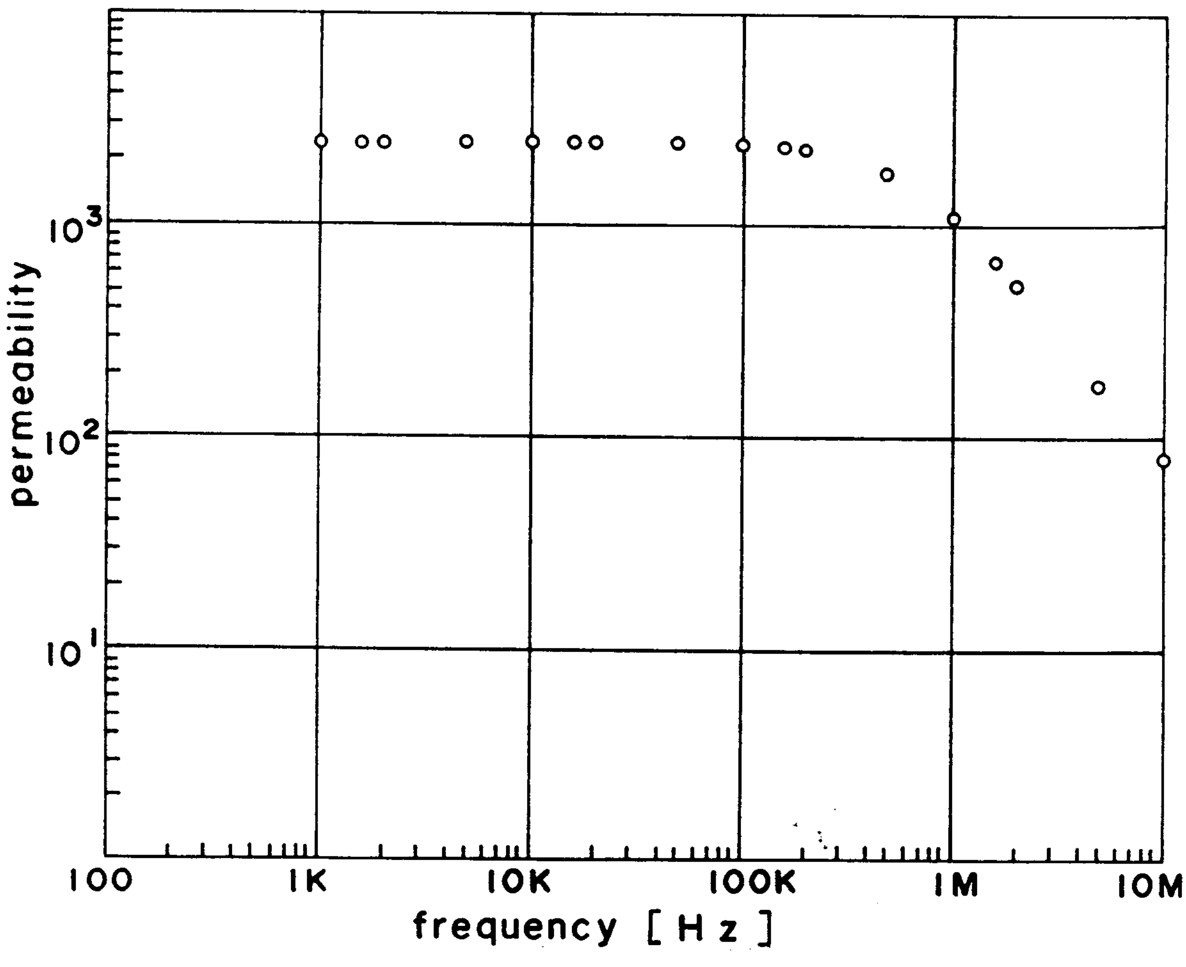

FIG.4

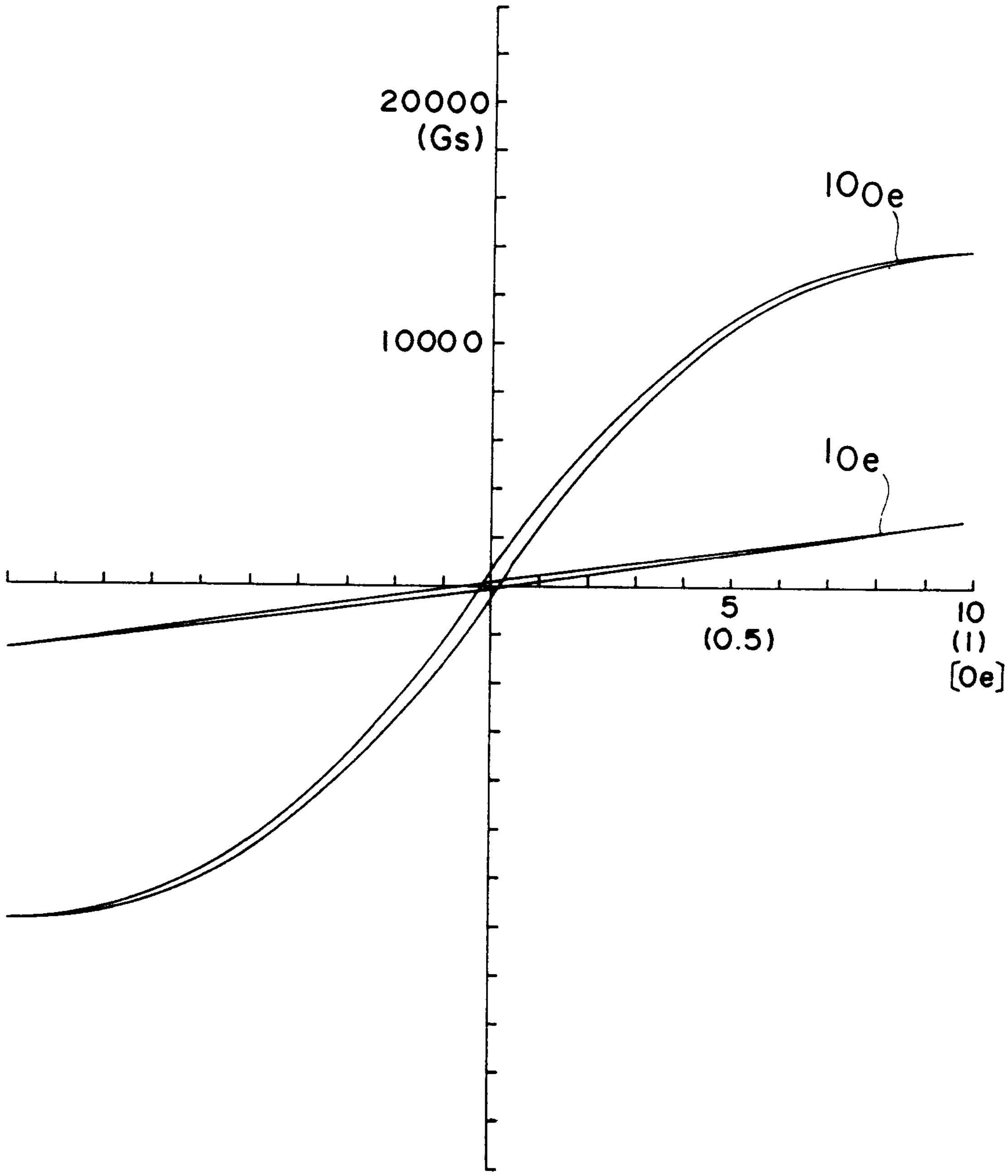

FIG.5

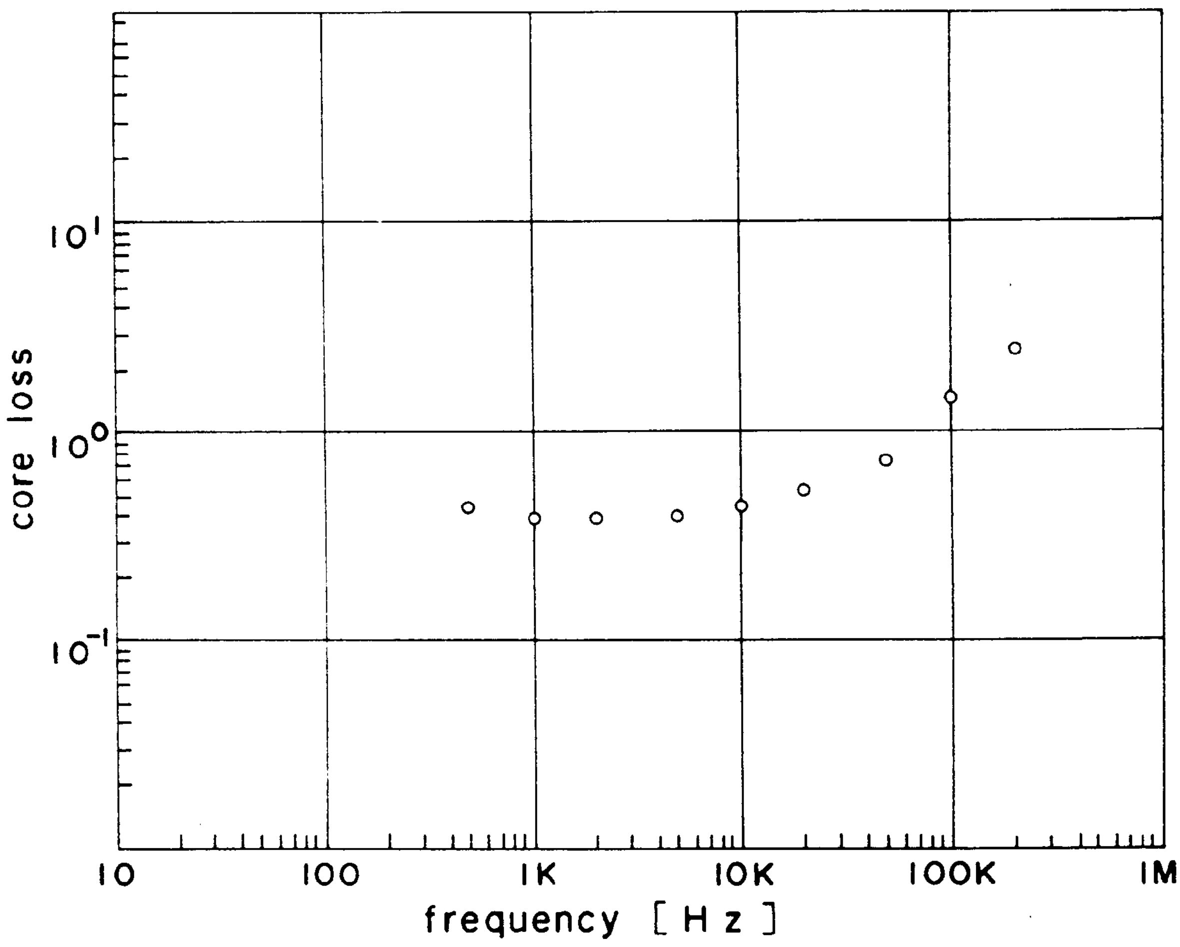

FIG.6

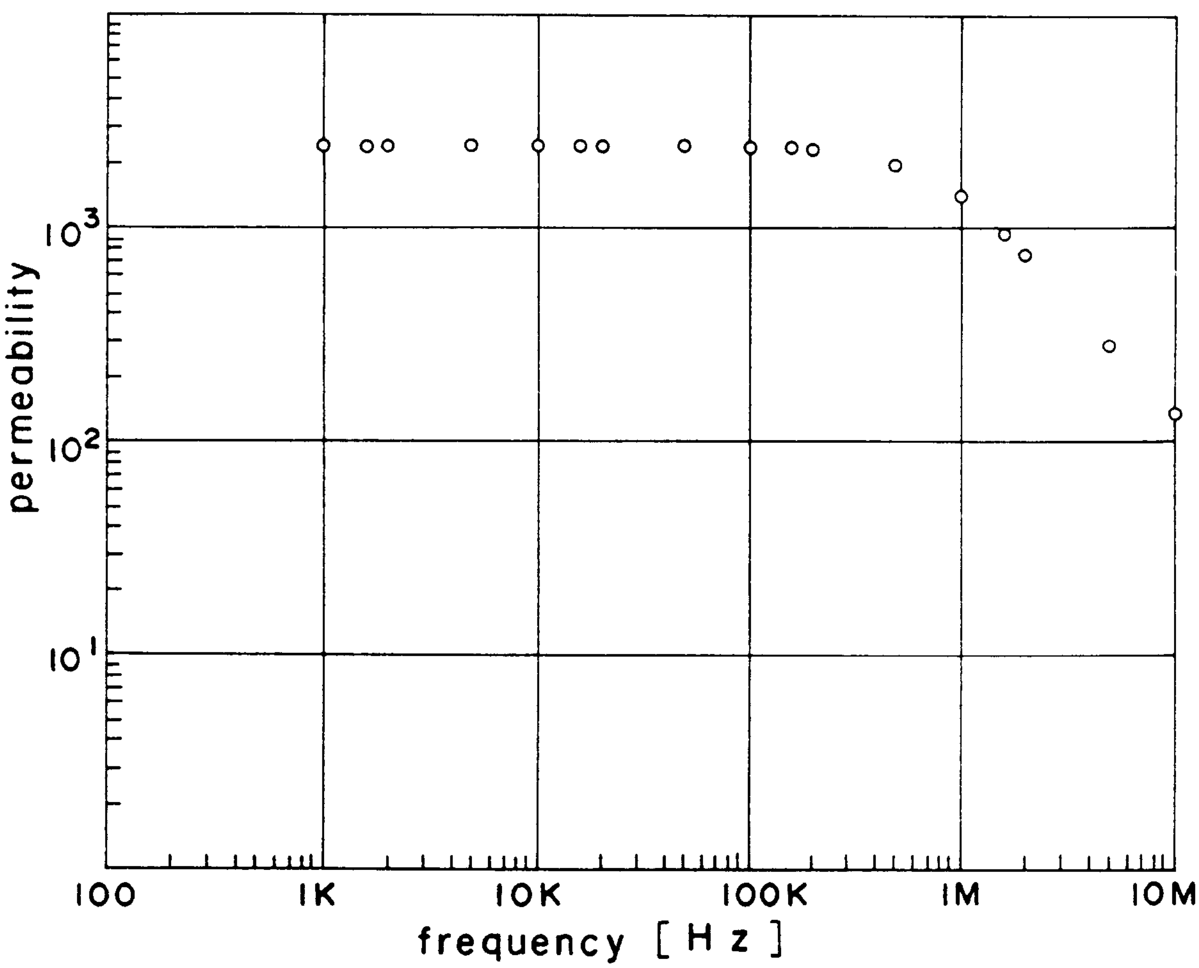

FIG.7

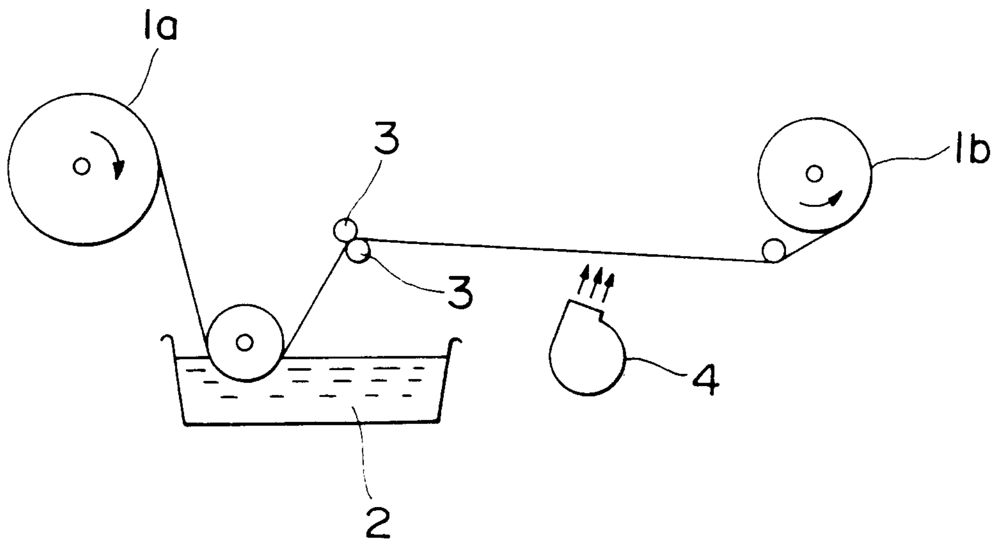

FIG.8