⑲ **Europäisches Patentamt**
European Patent Office
Office européen des brevets

⑪ Publication number: **0 639 848 A1**

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **93310036.4**

㉒ Date of filing: **13.12.93**

(51) Int. Cl.⁶: **H01J 1/14**

㉚ Priority: **20.08.93 KR 9316231**
19.10.93 KR 9321670
23.10.93 KR 9322124
27.10.93 KR 9322490

㊸ Date of publication of application:
22.02.95 Bulletin 95/08

(84) Designated Contracting States:
DE FR GB NL

(71) Applicant: **SAMSUNG DISPLAY DEVICES CO., LTD.**
575, Shin-ri,
Taean-eub
Hwaseong-gun,
Kyungki-do (KR)

(72) Inventor: **Choi, Jong-seo**
201-502, Baekjo Apt.,
Seoksu 1-dong
Anyang-city,
Kyungki-do (KR)
Inventor: **Shon, Kyung-cheon**
990, Maetan-dong,
Kwonsun-gu
Suwon-city,
Kyungki-do (KR)
Inventor: **Choi, Kwi-seok**
33-61, Junggok 3-dong
Seongdong-gu,
Seoul (KR)
Inventor: **Ju, Gyu-nam**
1/111, Samik Apt.,
Seocho-dong
Seocho-gu,
Seoul (KR)
Inventor: **Lee, Sang-won**
126/1301, Mugunghwa Apt.,
Keumjeong-dong
Kunpo-city,
Kyungki-do (KR)

(74) Representative: **Kyle, Diana**
Elkington and Fife
Prospect House
8 Pembroke Road
Sevenoaks, Kent TN13 1XR (GB)

(54) Oxide cathode for electron tube.

(57) In an oxide cathode comprising a metal base, an electron emissive material layer containing at least Ba formed on the metal base, and a means for heating the electron emissive material layer, the electron emissive material layer further comprises at least one of a lanthanum oxide and a terbium oxide, and forms a needle-shaped crystal structure, or the electron emissive material layer further comprises at least one of a lanthanum oxide and a terbium oxide, and the metal base is subject to a heat treatment under vacuum. The oxide cathode has an effect on lengthening the lifetime, and has a manufacturing procedure interchangeable with a conventional one.

Rank Xerox (UK) Business Services
(3.10/3.09/3.3.4)

Background of the Invention

The present invention relates to an oxide cathode for an electron tube such as a cathode ray tube or image pickup tube, and more particularly, to a novel oxide cathode for an electron tube having a long lifetime.

For a conventional thermoelectron emitting cathode for an electron tube, there is an "oxide cathode" which includes an alkaline earth metal carbonate layer formed on a metal base containing Ni as a main component. Such an alkaline earth metal carbonate is converted into oxide during an evacuating process and is therefore termed an oxide cathode. An oxide cathode works at relatively low temperatures (700-800 °C), since its work function is low. However, oxide cathodes have the problem of relatively short lifetimes.

FIG.1 is a schematic sectional view illustrating a structure of a conventional oxide cathode. A conventional oxide cathode comprises a disk-shaped metal base 2, a cylindrical sleeve 3 supporting the metal base 2, a heater 4 for heating the cathode, and an electron emissive material layer 1 which is formed on the metal base 2 and is made of an alkaline earth metal oxide as a main component. Such a conventional oxide cathode is manufactured by closing up one end of the cylindrical sleeve 3 with the metal base 2, inserting the heater 4 in the sleeve 3, and forming the electron emissive material layer 1 which is made of a mixture of at least two alkaline earth metal oxides on the surface of the base metal 2.

The metal base 2 is located on the sleeve 3 and supports the electron emissive material layer 1. It is made of a refractory metal, such as nickel (Ni) or platinum (Pt), and contains a reducing element to facilitate the reduction of an alkaline earth metal oxide. As a reducing element is typically used a reducing metal, such as tungsten (W), magnesium (Mg), silicon (Si) or zirconium (Zr). The reducing metals are generally used in combination with each other.

The sleeve 3, which supports the metal base 2 and has a heater 4 therein, is typically made of a refractory metal, such as molybdenum (Mo), tantalum (Ta), tungsten (W) or stainless steel.

The heater 4, which is located inside the sleeve 3, heats an electron emissive material layer 1 through the metal base 2. It is made of a tungsten wire coated with alumina et al.

The electron emissive material layer 1, which emits thermoelectrons, is formed on the metal base 2 as an alkaline earth metal oxide layer. A suspension of a carbonate of an alkaline earth metal (Ba, Sr, Ca etc.) is sprayed on the metal base 2. After the coating layer is heated by the heater 4 in a vacuum, the alkaline earth metal carbonate is converted to oxides. Barium carbonate, for example, decomposes to barium oxide as follows:

$$BaCO_3 \rightarrow BaO + CO_2 \uparrow$$

Then, the alkaline earth metal oxide is partially reduced at a high temperature of 900 to 1000 °C, so that it is activated to have semiconductive properties. In this activation process, the reducing element, such as Si or Mg, contained in the metal base 2 diffuses to move toward the interface between the electron emissive material layer 1 composed of the alkaline earth metal oxide and the metal base 2, and then reacts with the alkaline earth metal oxide. For example, barium oxide is reduced by the reducing element to give free barium.

$$BaO + Mg \rightarrow MgO + Ba \uparrow$$
$$4BaO + Si \rightarrow Ba_2SiO_4 + 2Ba \uparrow$$

The free barium derived from BaO becomes a semiconductor of an oxygen vacancy type. Consequently, an emission current of 0.5 to 0.8A/cm^2 is obtained under the normal condition at an operation temperature of 700 to 800 °C.

Generally, an oxide cathode operates at high temperature over 750 °C, so free Ba, Sr or Ca vaporizes due to the high vapor pressure and an electron emissive surface reduces while operating. In addition, as a result of a reduction of the alkaline earth metal oxide, an intermediate layer of an oxide, such as MgO or Ba_2SiO_4, is formed in the interface region between the electron emissive material layer and the metal base and serves as a barrier. The barrier so formed prevents the reducing element Mg or Si from diffusing into the electron emissive layer, so that a sufficient amount of a free Ba cannot be generated and the vaporized Ba, Sr or Ca is hard to be refilled. Further, electron emissive current is also limited by a high resistance of the intermediate layer. Therefore, the intermediate layer contributes to the shortening of the cathode lifetime and other undesirable results. On the other hand, an excessive supply of the reducing element results in excessive reduction of BaO, so that stable emission cannot be achieved.

As described above, a conventional oxide cathode has disadvantages in that its operation temperature becomes higher during use, so the emission efficiency decreases to about 75% of initial characteristic, and the exhaustion of electron emissive material shortens its lifetime.

Recent progress toward the enlargement and high qualification of the picture tube requires a high luminance and fineness of the tube. Accordingly, a cathode of an electron gun needs to give an electron emission of a high current density and have a long lifetime. However, a conventional oxide cathode has a short lifetime in general, so it cannot satisfy such requirements.

An impregnated-type cathode, known to have a high current density and a long lifetime, is manufactured by a complicated process and the operation temperature is 1100 ° C or higher, which is as much as 300-400 ° C higher than that of an oxide cathode. Therefore, continuous efforts have been made to lengthen the lifetime of an oxide cathode, which can be manufactured easily and operates at low temperature.

In Japanese Patent Laid-open Publication No. sho 59-20941, lanthanum is dispersed in a metal base in the form of $LaNi_5$ and La_2O_3, so that the strength of the metal base is not weakened and the reducing agent therein is not exhausted. British Patent No. 1592502 discloses an electron emissive material for a discharge lamp in which BeO and Y_2O_3 are added to $Ba_{2-x}Sr_xCaWO_6$ (where x is from 0.0 to 0.5).

In United States Patent No. 4,797,593, at least one rare earth metal oxide selected from the group consisting of the oxides of Y, La, Ce, Pr, Nd, Sm, Gd, Sc, Dy, Ho, Er and Tm, is added to the electron emissive substance containing at least Ba, in order to improve the electron emission characteristic.

The above-mentioned cathodes, however, do not make a considerable improvement in the short lifetime of an oxide cathode. Further, the manufacturing processes of the above cathode is not always interchangeable with those of the typical oxide cathode. Especially, changing the activation process of the cathode is required. For example, in the above US patent (No. 4,797,593), the rare earth metal oxide needs to be subjected to a heat treatment at a high temperature in a reducing atmosphere before mixing with an alkaline earth metal oxide.

Summary of the Invention

An object of the present invention considering the above-mentioned problems of the conventional oxide cathodes is to provide an oxide cathode in which a stable electron emissive characteristic is maintained for a longer time by suppressing an excessive Ba vaporization, so that the lifetime has been greatly improved, and the manufacturing process is interchangeable with a conventional one.

To accomplish the object, there is provided an oxide cathode according to an embodiment of the present invention, comprising:

a metal base;

an electron emissive material layer containing at least Ba formed on the metal base; and

means for heating the electron emissive material layer,

characterized in that the electron emissive material layer further comprises at least one of a lanthanum oxide and a terbium oxide, and forms a needle-shaped crystal structure.

To accomplish the object, there is also provided an oxide cathode according to another embodiment of the present invention, comprising:

a metal base;

an electron emissive material layer containing at least Ba formed on the metal base; and

means for heating the electron emissive material layer,

characterized in that the electron emissive material layer further comprises at least one of a lanthanum oxide and a terbium oxide, and that the metal base is subject to heat treatment under a vacuum.

The amount of the lanthanum oxide or the terbium oxide contained in the electron emissive material layer is preferred to be in the range of 0.0001% to 5% by weight, based on the total amount of the electron emissive material.

In addition, the oxide cathode according to another embodiment of the present invention, a metal base is preferred to be subjected to a heat treatment at the temperature over 900 ° C, under a vacuum of over 10^{-6} torr.

Brief Description of the Drawings

The above objects and other advantages of the present invention will become more apparent by describing in detail a preferred embodiment thereof with reference to the attached drawings in which:

FIG.1 is a schematic sectional view illustrating a conventional oxide cathode;

FIG.2 is an enlarged schematic view illustrating an electron emissive material layer of an oxide cathode according to an embodiment of the present invention;

FIG.3 is a graph showing MIK change with respect to the time passage of an oxide cathode according to an embodiment of the present invention (a) and a conventional oxide cathode (b); and

FIG.4 is a graph showing MIK change with respect to the time passage of an oxide cathode according to another embodiment of the present invention (a) and a conventional oxide cathode (b).

Detailed Description of the Invention

In an oxide cathode according to the present invention, an electron emissive material layer on a metal base further contains a lanthanum oxide and/or a terbium oxide, and the electron emissive material layer forms a needle-shaped crystal structure, or the metal base is subject to a heat treatment under vacuum, so that the electron emissive characteristic becomes stable and the emission stability is maintained longer than that of conventional ones.

Lanthanum oxide and/or terbium oxide added to the electron emissive materials containing at least Ba forms a stable BaO in the electron emissive material layer after an aging process, so that the cathode has a stable electron emission characteristic.

In addition to the stable electron emission characteristic due to the stable BaO, an adequate supply of a reducing metal has been considered in order to lengthen the lifetime of an oxide cathode. Such an adequate supply of a reducing metal may be achieved according to the following two methods. The first is to form a needle-shaped crystal structure of the electron emissive material layer, and the second is a heat treatment of the metal base. If an electron emissive material layer forms a needle-shape crystal, a reducing metal may diffuse at an adequate speed, so that a current density may be kept up with an enhanced value for a long time. Alternatively, if a metal base containing a reducing metal is subject to the heat treatment under vacuum, the excessive supply of the reducing metal may be prevented, so that stable BaO produced by the lanthanum oxide and/or terbium oxide may keep its stable condition over a long period of time. In this manner, an electron emission may be stabilized for a long time and the lifetime of the oxide cathode may be increased.

In the present invention, as an electron emissive material may be used a triple carbonate, such as $(Ba,Sr,Ca)CO_3$, or a double carbonate, such as $(Ba,Sr)CO_3$. In order to add lanthanum oxide or terbium oxide to an electron emissive material, any lanthanum compound or terbium compound which can be converted to oxide by heating may be used as well as lanthanum oxide or terbium oxide itself.

The amount of lanthanum oxide or terbium oxide contained in an electron emissive material is preferred to be in the range of 0.0001% to 5% by weight, based on the total amount of the electron emissive material. Lanthanum oxide or terbium oxide of less than 0.0001% by weight cannot achieve the effect of forming the stable BaO, and so does not lengthen the lifetime. On the other hand, lanthanum oxide or terbium oxide of more than 5% by weight may aggravate the already poor condition of the initial emission characteristic and thus decrease the effect of lengthening the lifetime.

Lanthanum oxide or terbium oxide, or both is contained in, for example, a co-precipitated triple carbonate of $(Ba,Sr,Ca)CO_3$ as an electron emissive material. The co-precipitated triple carbonate is conventionally manufactured by dissolving nitrates such as $Ba(NO_3)_2$, $Sr(NO_3)_2$ or $Ca(NO_3)_2$ in pure water, and adding Na_2CO_3 or $(NH_4)_2CO_3$ as a precipitant to the nitrate solution to co-precipitate as a carbonate of Ba, Sr and Ca. At this manufacturing process, in accordance with such factors as the concentration of nitrates, the pH value, the solution temperature at precipitation or the precipitation speed, the obtained carbonate crystal structures vary. According to an embodiment of the present invention, the above factors should be controlled to form a needle-shaped crystal structure. To the co-precipitated triple carbonate electron emissive material of a needle-shaped crystal, lanthanum oxide and/or terbium oxide, or lanthanum compound and/or terbium compound which may be converted to oxide by heating is added to create a suspension. The suspension may be applied onto a metal base by means of dipping, spraying or sputtering to give an oxide cathode according to one embodiment of the present invention.

In an oxide cathode according to another embodiment of the present invention, a metal base is preferred to be subjected to heat treatment at a temperature over 900 °C, under a vacuum of over 10^{-6} torr. Also, lanthanum oxide and/or terbium oxide is contained in, for example, a co-precipitated triple carbonate of $(Ba,Sr,Ca)CO_3$ as an electron emissive material.

The oxide cathode of the present invention is inserted and fixed in an electron gun, and a heater is inserted and fixed in a sleeve. After the electron gun is sealed into a bulb for an electron tube, the carbonate of the electron emissive material layer is decomposed to the oxide by the heater during an evacuating process. Thereafter, an activation process is carried out by a conventional manufacturing process for an electron tube.

The present invention will be described in detail by way of the following examples which are merely representative and illustrative of the present invention and are in no way to be considered as limiting the invention to the specific examples.

(Example 1)

To the solution of a mixture of $Ba(NO_3)_2$, $Sr(NO_3)_2$ and $Ca(NO_3)_2$, in which the ratio of Ba:Sr:Ca was 50:40:10, ammonium carbonate was added to form a co-precipitated carbonate of Ba, Sr and Ca. At this time, in order to form a co-precipitated triple carbonate of a needle-shaped crystal structure, the reaction condition was controlled as follows: the concentration of the triple nitrates was above 0.6M; pH was controlled to be above 8 with ammonium hydroxide; and, when $(NH_4)_2CO_3$ was used as a precipitant, the temperature of the nitrate solution was above 60 ° C, and the solution of precipitant was dropped at the speed of 30ml per minute. To the co-precipitated triple carbonate of a needle-shaped crystal structure, La_2O_3 was added in the amount of 1% by weight of the electron emissive material calculated as oxide. Further, a nitrocellulose and an organic solvent were dispersed to make a suspension of the electron emissive material.

A Ni-metal base containing Si and Mg was washed. Then, the above manufactured suspension of the electron emissive material was spray-coated on the base, dried to obtain an oxide cathode according to an embodiment of the present invention.

(Example 2)

The same procedure as in Example 1 was repeated, except that Tb_4O_7 was added to the co-precipitated triple carbonate solution in the amount of 5% by weight of the electron emissive material calculated as oxide, to obtain an oxide cathode according to an embodiment of the present invention.

(Example 3)

The same procedure as in Example 1 was repeated, except that La_2O_3 was added to the co-precipitated triple carbonate solution in the amount of 0.0001% by weight of the electron emissive material calculated as oxide, to obtain an oxide cathode according to an embodiment of the present invention.

(Example 4)

The same procedure as in Example 1 was repeated, except that Tb_4O_7 was added to the co-precipitated triple carbonate solution in the amount of 0.001% by weight of the electron emissive material calculated as oxide, to obtain an oxide cathode according to an embodiment of the present invention.

(Example 5)

The same procedure as in Example 1 was repeated, except that the mixture of La_2O_3 and Tb_4O_7 was added to the co-precipitated triple carbonate solution in the amount of 0.01% by weight of the electron emissive material calculated as oxide, to obtain an oxide cathode according to an embodiment of the present invention.

(Example 6)

A Ni-metal base containing Si and Mg was subjected to heat treatment at 1000 ° C, under a vacuum of over 10^{-6} torr.

To an electron emissive material of a co-precipitated triple carbonate, La_2O_3 was added in the amount of 1% by weight of the electron emissive material calculated as oxide. Further, a nitrocellulose and an organic solvent were dispersed to make a suspension of an electron emissive material.

The above suspension was spray-coated on the heat-treated metal base, and dried to obtain an oxide cathode according to another embodiment of the present invention.

(Example 7)

The same procedure as in Example 6 was repeated, except that La_2O_3 was added to the co-precipitated triple carbonate solution in the amount of 0.0001% by weight of the electron emissive material calculated as oxide, to obtain an oxide cathode according to another embodiment of the present invention.

(Example 8)

The same procedure as in Example 6 was repeated, except that $La_2O_3$was added to the co-precipitated triple carbonate solution in the amount of 5% by weight of the electron emissive material calculated as oxide, to obtain an oxide cathode according to another embodiment of the present invention.

FIG.2 is an enlarged schematic view illustrating an electron emissive material layer of an oxide cathode manufactured according to Example 1. FIG.2 shows that the electron emissive material manufactured in Example 1 forms a needle-shaped crystal structure.

In order to evaluate the characteristics of the oxide cathode of the present invention, the oxide cathode manufactured according to the above is inserted and fixed in an electron gun, and a heater is inserted and fixed in a sleeve. After the electron gun is sealed into a bulb for an electron tube, the carbonate of the electron emissive material layer is decomposed to the oxide by the heater during an evacuating process. Thereafter, an activation process is carried out by a conventional manufacturing process for an electron tube, and its electron emissive characteristic is measured.

An initial electron emission characteristic is evaluated by MIK (maximum cathode current) which is the maximum current emitted by a cathode under a constant operating condition. A lifetime characteristic is evaluated by the amount of decrease in the current when a cathode installed in an electron tube is operated continuously for a ccertain length of time under constant conditions. That is, it is evaluated in terms of MIK consistency for a constant period.

FIG.3 is a graph showing MIK change with respect to the time of the oxide cathode manufactured according to Example 1 (a) and a conventional oxide cathode (b). As shown in FIG.3, an oxide cathode according to an embodiment of the present invention has an effect on lengthening lifetime by 20% more than a conventional one. The oxide cathodes manufactured according to Examples 2 through 5 also show that they have equal effects on the lifetime.

FIG.4 is a graph showing MIK change with respect to the time of an oxide cathode manufactured according to Example 6 (a) and a conventional oxide cathode (b). As shown in FIG.4, an oxide cathode according to another embodiment of the present invention has an effect on lengthening lifetime by 20% more than a conventional one. The oxide cathodes manufactured according to Examples 7 and 8 also show that they have equal effects on the lifetime.

As shown above, the oxide cathode according to the present invention, which is characterized in that the electron emissive material layer contains a lanthanum oxide and/or a terbium oxide and forms a needle-shaped crystal structure, or which is characterized in that the electron emissive material layer contains a lanthanum oxide and/or a terbium oxide and that the metal base is subject to a heat treatment under vacuum, has an effect on lengthening the lifetime, and has a manufacturing procedure interchangeable with a conventional one.

While the present invention has been particularly shown and described with reference to particular embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be effected therein without departing from the spirit and scope of the invention as defined by the appended claims.

Claims

1. An oxide cathode comprising:

a metal base;

an electron emissive material layer containing at least Ba formed on the metal base; and

means for heating the electron emissive material layer,

characterized in that the electron emissive material layer further comprises at least one of a lanthanum oxide and a terbium oxide, and forms a needle-shaped crystal structure.

2. An oxide cathode as claimed in claim 1, wherein the amount of at least one of a lanthanum oxide and a terbium oxide is in the range of 0.0001 % to 5% by weight, based on the total amount of the electron emissive material.

3. An oxide cathode comprising:

a metal base;

an electron emissive material layer containing at least Ba formed on the metal base; and

means for heating the electron emissive material layer,

characterized in that the electron emissive material layer further comprises at least one of a lanthanum oxide and a terbium oxide, and that the metal base is subject to a heat treatment under vacuum.

4. An oxide cathode as claimed in claim 3, wherein the amount of at least one of a lanthanum oxide and a terbium oxide is in the range of 0.0001% to 5% by weight, based on the total amount of the electron emissive material.

5. An oxide cathode as claimed in claim 3, wherein the metal base is subjected to heat treatment at a temperature over 900 °C, under a vacuum of over 10^{-6} torr.

FIG. 1

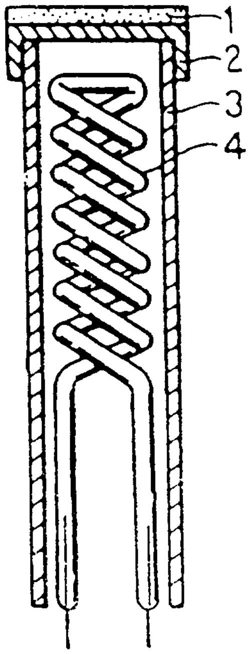


FIG. 2

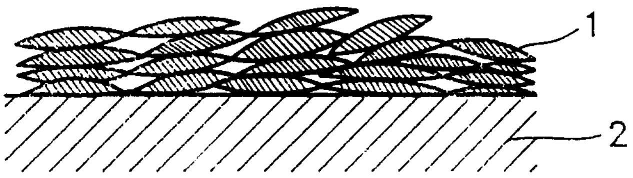


FIG. 3

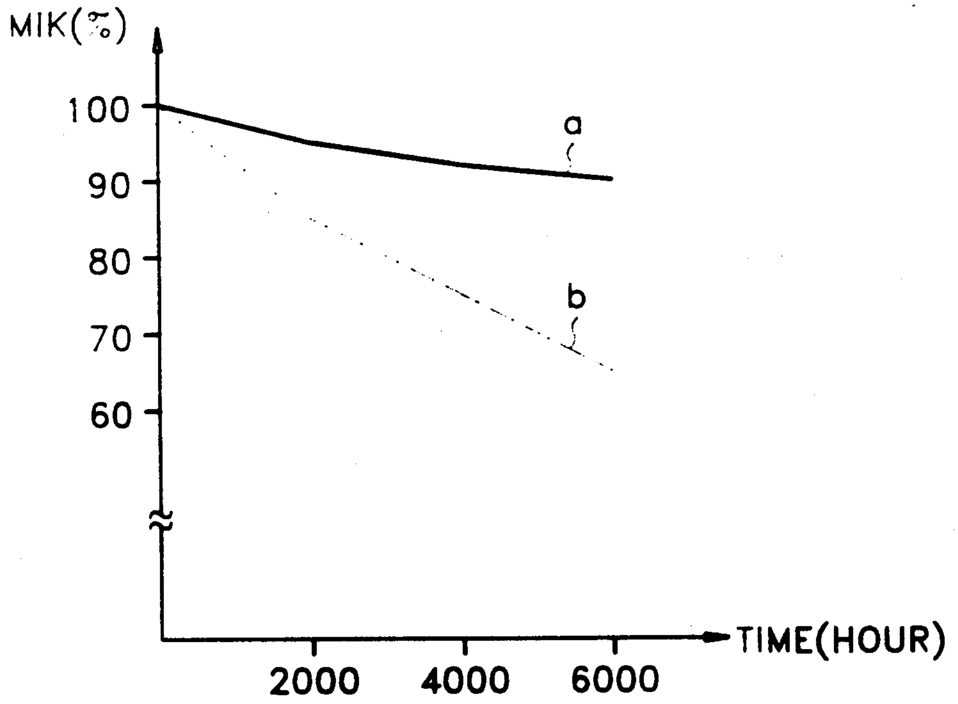
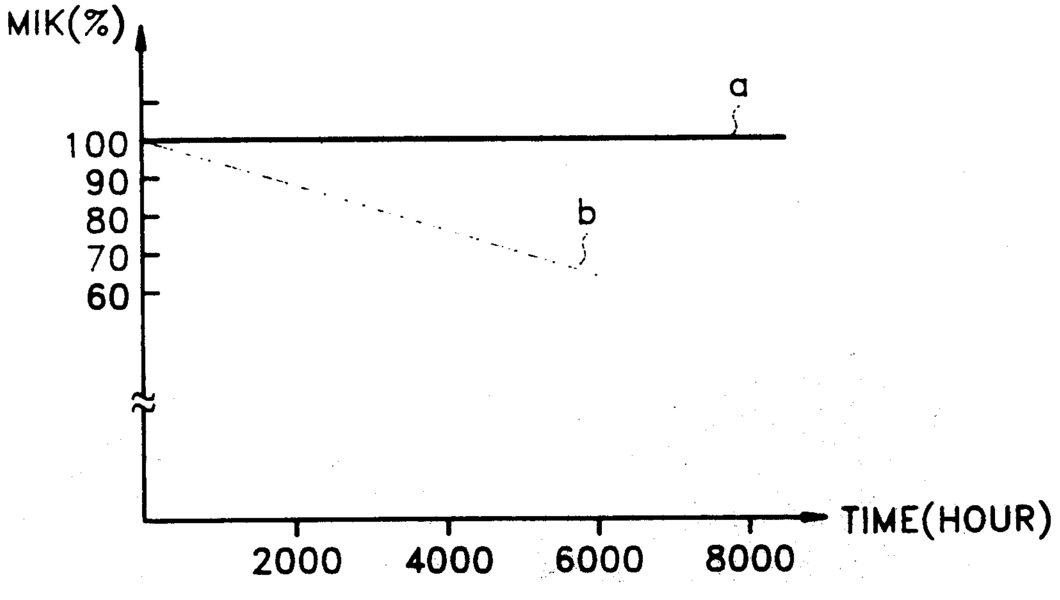

MIK(%)
100
90
80
70
60
a
b
2000
4000
6000
TIME(HOUR)

FIG. 4


MIK(%)
100
90
80
70
60
a
b
2000
4000
6000
8000
TIME(HOUR)

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 31 0036

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-1 794 298 (A.JUST) * page 2, line 18 - line 25; claims 1,2 * ---	1	H01J1/14
X	GB-A-182 817 (GESELLSCHAFT FUR DRAHTLOSE TELEGRAPHIE M.B.H.) ---	1	
D,X	US-A-4 797 593 (M.SAITO ET AL.) * claim 1 * -----	1,2	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			H01J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 November 1994	Van den Bulcke, E

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document