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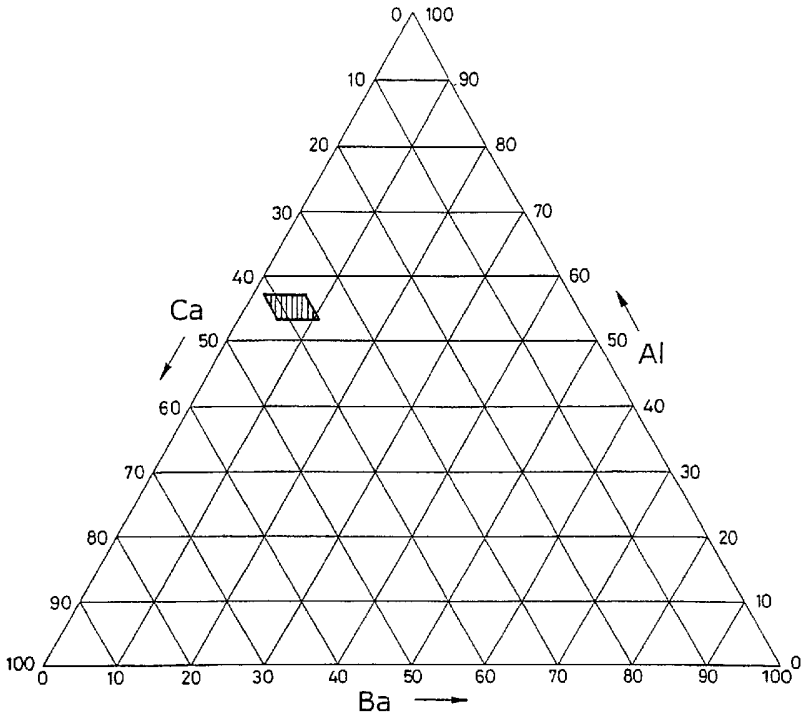
(54) **Title:** GETTER ALLOYS AND DEVICES FOR EVAPORATING CALCIUM



(57) **Abstract:** There are described evaporable getter devices for evaporating calcium, based on use of Ca-Ba-Al ternary alloys containing from 53% to 56.8% by weight of aluminium, from 36% to 41.7% by weight of calcium and from 1.5% to 11% by weight of barium.

WO 03/038139 A1

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

"GETTER ALLOYS AND DEVICES FOR EVAPORATING CALCIUM"

The present invention relates to alloys for evaporating calcium and to getter devices which make use of these alloys to evaporate calcium inside systems working under vacuum, in particular cathodic tubes.

A number of industrial applications require a suitable vacuum degree to be kept in a sealed space for a period of several years. It is for example the case of the cathodic tubes, also known in the field as CRTs (from Cathode Ray Tubes), that are used as screens of television sets or computers. In CRTs vacuum is required to avoid the path of electrons emitted by a cathode being deflected through a collision with gas particles. CRTs are evacuated during the manufacturing step through mechanical pumps and then hermetically sealed; a vacuum in the tube tends however to decrease during time, mainly because of the degassing from internal components of the tube. It is therefore necessary to use inside the tube a getter material capable of capturing the gaseous molecules thus keeping the vacuum degree necessary for the cathodic tube to work. To this purpose barium is usually used in the form of a thin film deposited on inner walls of the cathodic tube. Because of the high reactivity of this metal, which would make every manufacturing operation troublesome, barium is used in the form of the air stable compound $BaAl_4$. To introduce the compound inside the cathodic tube there are utilized the so called "evaporable getter" devices, formed of an open metallic container, inside which there is a compressed mixture of $BaAl_4$ and nickel powders (in a weight ratio of about 1:1); devices of this type are disclosed for example in patents US 2,842,640, 2,907,451, 3,033,354, 3,225,911, 3,381,805, 3,719,433, 4,134,041, 4,486,686, 4,504,765, 4,642,516 and 4,961,040.

These devices are introduced inside the cathodic tube before sealing it, and then are heated from outside through radio frequencies to cause the evaporation of barium, which then condenses on the internal walls thus forming the film active in sorbing gases. Nickel has the function of reducing the energy required at radio-frequency heating: when the temperature of the mixture reaches about 850 °C, the following exothermal reaction takes place:

$BaAl_4 + 4\ Ni \rightarrow Ba + 4\ NiAl$

The heat generated by this reaction raises the temperature of the system up to about 1200 °C, necessary to have barium evaporation; these devices are defined "exothermal" in the field.

The use of barium, however, has some drawbacks.

First of all, like all heavy metals, it is a toxic element, so that the use thereof imposes special precautions in every manufacturing step of the compound $BaAl_4$, as well as in disposing the CRTs at the end of their life in order to avoid ecological problems due to dispersion of the element in the environment.

Furthermore, inside the cathodic tubes, barium is present also in areas hit by highly energetic electron beams used to generate the image inside the kinescope; in these conditions barium, and consequently the screen of the kinescope, emit X rays (even though in small quantities) that are notoriously harmful to health.

In order to avoid the problems caused by the use of barium, the international patent application WO 01/01436 proposes using calcium as a gas sorbing element, and the compound $CaAl_2$ as a precursor to be utilized for evaporating calcium. The compound $CaAl_2$ is preferably used in mixture with titanium powders.

The use of calcium-based evaporable getter devices has also some advantages during the manufacture of CRTs, in that the evaporation of calcium is less violent and more easily controllable with respect to barium, even after the treatments at relatively high temperatures (about 450 °C) in oxidizing atmosphere which occur during some manufacturing steps of the tubes.

The calcium based devices of the mentioned international patent application have however the problem that the compound $CaAl_2$ accumulates, during its manufacture, more hydrogen than in the case of $BaAl_4$. The hydrogen contained in the compound is released during the evaporation of the metal, and it can negatively interfere with this operation; furthermore, it is known in the field that hydrogen can react with carbon atoms on the surface of these metallic films thus forming mainly methane, which is reabsorbed only with difficulty and partially by the same film.

The object of the present invention is to provide getter devices for

evaporating calcium which do not have the problems of analogous known devices.

These objects are achieved according to the present invention through ternary alloys Ca-Ba-Al containing between 53% and 56.8% by weight of aluminum, between 36% and 41.7% by weight of calcium and between 1.5% and 11% by weight of barium and through devices containing these alloys.

The invention will be described below with reference to the drawings, in which:

- figure 1 shows a ternary diagram wherein the possible compositions of the alloys according to the present invention are illustrated;

- figure 1a shows an enlargement of the diagram of figure 1, in its relevant part;

- figure 2 shows the progress of the amount of hydrogen released by comparative devices and by the inventive devices as a function of the quantity of barium present in the alloy utilized in preparing the device.

The inventors have found that by substituting in compound $CaAl_2$ a small fraction of calcium atoms with barium atoms it is possible to reduce, until it becomes negligible, the problem of the hydrogen release during the calcium evaporation step.

The alloys of the invention are ternary alloys Ca-Ba-Al with a content varying between 53% and 56.8% by weight of aluminum, between 36% and 41.7% by weight of calcium and between 1.5% and 11% by weight of barium. These compositions fall within the dashed area of the ternary diagram of figure 1; this area having the form of a parallelogram is shown in figure 1a, wherein some compositions produced and tested in the examples are also indicated. At barium weight percentages lower than 1.5% there is not seen a noteworthy reduction of the released hydrogen amount with respect to compound $CaAl_2$. At barium weight percentages higher than 11% there is not seen a further reduction of hydrogen emission; Ca-Ba-Al alloys with a higher barium percentage could well be utilized, but they would have the drawback of increasing the amount of a potentially toxic element, not compensated by advantages regarding hydrogen emission. Within this range, alloys with a content of barium included between 2.5% and 5% by

weight, are preferred.

With reference to compound $CaAl_2$, it is possible to produce alloys wherein as the barium percentage by weight increases, only the calcium percentage correspondingly decreases, while the aluminum percentage remains constant; preferably however also the aluminum content is decreased as the barium percentage increases.

The alloys of the invention are simply prepared by smelting the component metals in a stoichiometric ratio. The melting can be carried out in a furnace of any type, for example an induction one, and preferably under an inert atmosphere, for example nitrogen.

In industrial applications, the alloys of the invention can be utilized in evaporable getter devices, formed of a container made up of metal, generally steel. The container is open on the upper part and has generally the shape of a short cylinder (in the case of the smaller devices) or of an annular channel with an essentially rectangular cross-section. The shape of the container can be essentially the same as the shape of containers utilized for analogous known devices, as described in US patents mentioned before.

These devices can be of the so-called "endothermic" type, wherein the whole heat necessary for the calcium evaporation is to be provided from outside, generally through induction heating; devices of this type contain only a compound of the invention. Preferably however devices of "exothermic" type are used, as described previously with reference to devices for evaporating barium, containing, apart from an alloy of the invention, nickel, titanium, or mixtures of powders of these two metals; the use of titanium is preferred.

Inside these devices the alloy Ca-Ba-Al is preferably used in the form of powders, generally with a granulometry lower than about 500 μm, preferably lower than 250 μm, and still more preferably included between about 45 and 150 μm.

In the case of exothermic devices, nickel or titanium are preferably utilized in the form of powders having a granulometry lower than about 100 μm and still more preferably included between about 20 and 70 μm.

The weight ratio between the alloy Ca-Ba-Al and Ni or Ti in exothermic devices can vary within a wide range: this ratio can be included between about 1:3 and 3:1 and is preferably about 1:1.

Also in the devices of the invention it is possible to have recourse to the teachings of the prior art, concerning barium evaporable getters, to improve the performances.

For example, the device can contain percentages up to about 5% by weight (on the mixture of powders) of a compound chosen among iron nitride, germanium nitride or mixtures thereof; in these devices nitrogen is released just before the evaporation of calcium, which allows to obtain a more diffused metal film having a more homogeneous thickness. Examples of nitrogen containing devices are reported in patents US 3,389,288 and 3,669,567.

The free surface of the packet of powders in the container, both in the case of endothermic and exothermic devices, can have radial depressions (from 2 to 8, normally 4) to moderate the transfer of heat in the circular sense in the packet, thus reducing the problem of a possible expulsion of solid particles during calcium evaporation. For a more detailed explanation of this problem, and of the solution provided by the radial depressions, it is to be referred to patent US 5,118,988.

Finally, in order to improve the homogeneity of the inductive heating of the packet of powders, it is possible to add in the packet a discontinuous metallic element, essentially parallel to the bottom of the container, as described in patent US 3,558,962 and in European patent application EP-A-853328.

The invention will be further explained by the following examples. These non-limiting examples illustrate some embodiments aiming at teaching to those skilled in the art how to put the invention into practice and to represent the best regarded mode to realize the invention.

EXAMPLE 1 (COMPARATIVE)

100 g of compound $CaAl_2$ are prepared by smelting in a refractory crucible (made of mixed oxides of aluminum and magnesium) 42.6 g of calcium in the form of chips and 57.4 g of aluminum in the form of drops. In the portion of the

ternary diagram of figure 1a, this composition is represented by an empty circle. The melting is carried out in an induction furnace under nitrogen. After the solidification of the melt product, the ingot is ground and the powders are sifted, recovering the fraction with granulometry included between 45 and 150 μm. 49.5 g of this powder are mixed with 50.5 g of titanium powder having a mean granulometry of 40 μm. With this mixture five devices for evaporating calcium are prepared, by using for each one a steel container shaped as an annular channel, with outer diameter of 20 mm and channel width of 6 mm; each container is filled up with 1 g of mixture, compressing the powders with a shaped punch to which a pressure of about 6500 Kg/cm^2 is applied.

EXAMPLE 2 (COMPARATIVE)

According to the same procedure of example 1, 100 g of a ternary alloy with a per cent composition by weight Ca 42.3% - Ba 0.5% - Al 57.2%; this composition corresponds to an empty circle in the portion of the ternary diagram of figure 1a. The ingot is ground recovering the fraction having a granulometry included between 45 and 150 μm; 45 g of powder so obtained are mixed with 55 g of titanium powder having a mean granulometry of 40 μm, and with this mixture five devices for evaporating calcium are prepared.

EXAMPLE 3

Five getter devices for evaporating calcium are manufactured following the procedure of example 2, by using however an alloy with a per cent composition by weight Ca 41.7% - Ba 1.5% - Al 56.8%. This composition corresponds to point A, represented with a filled square, in figure 1a.

EXAMPLE 4

Five getter devices for evaporating calcium are manufactured following the procedure of example 2, by using however an alloy with a per cent composition by weight Ca 41.1% - Ba 2.5% - Al 56.4%. This composition corresponds to point B, represented with a filled square, in figure 1a.

EXAMPLE 5

Five getter devices for evaporating calcium are manufactured following the procedure of example 2, by using however an alloy with a per cent composition

by weight Ca 39.5% - Ba 5% - Al 55.5%. This composition corresponds to point C, represented by a filled square, in figure 1a.

EXAMPLE 6

Five getter devices for evaporating calcium are manufactured following the procedure of example 2, by using however an alloy with a per cent composition by weight Ca 36% - Ba 11% - Al 53%. This composition corresponds to point D, represented with a filled square, in figure 1a.

EXAMPLE 7

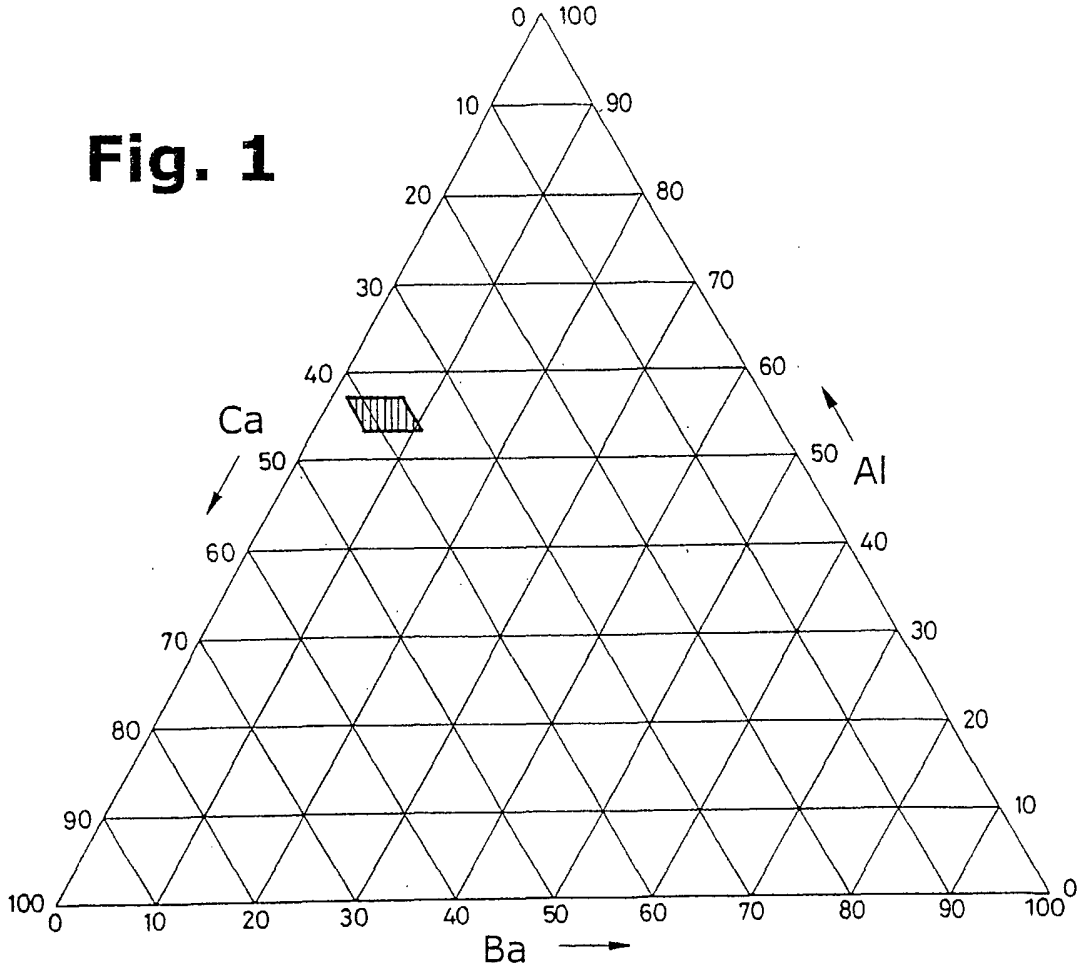
The series of five evaporable getter devices produced in each of the examples from 1 to 6 (totally 30 devices) are subjected to evaporation tests. The samples are introduced one at a time in a glass flask with a volume of 6 l, vacuum is made in the flask (pressure lower than 10^{-8} mbar) and the getter device is heated from outside by induction through radio-frequency. The flask is connected to a mass spectrometer, which records the development of the hydrogen pressure in the flask during time. This pressure has a maximum value corresponding to the evaporation and then decreases due to the reabsorption by the calcium film produced on the inner walls of the flask. According to an usual procedure in the field of evaporable getters, the evaluation of the hydrogen pressure is effected 15 minutes after the evaporation. It is made an average of the results from the five tests carried out for each composition. The average values so obtained are shown in the semilogarithmic graph of figure 2, wherein the common logarithm of the hydrogen pressure value (in mbar) 15 minutes after the evaporation is reported as a function of the percentage by weight of barium in the sample; the values corresponding to the comparative samples are represented with an empty circle and the values corresponding to the four samples of the invention with a filled square.

As it is noted from the examination of figure 2, devices prepared with alloys of the invention present, short after the evaporation of calcium, a low hydrogen release of about 10^{-5} mbar or less, that is compatible with the expected application in the manufacturing of CRTs for television sets and computer screens.

CLAIMS

1. Ca-Ba-Al ternary alloys containing between 53% and 56.8% by weight of aluminum, between 36% and 41.7% by weight of calcium and between 1.5% and 11% by weight of barium.
2. Alloys according to claim 1, wherein the barium content is included between 2.5% and 5% by weight.
3. A getter device for evaporating calcium formed of a metallic container open at the upper part, wherein a packet of compressed powders of an alloy of claim 1 is present.
4. Getter device according to claim 3, wherein said powders have a granulometry lower than 500 μm.
5. Getter device according to claim 4, wherein said powders have a granulometry lower than 250 μm.
6. Getter device according to claim 4, wherein said powders have a granulometry included between 45 and 150 μm.
7. Getter device according to claim 3, wherein said packet of powders further contains powders of a metal chosen among nickel and titanium or a mixture thereof.
8. Getter device according to claim 7, wherein said metal powders have a granulometry lower than 100 μm.
9. Getter device according to claim 8, wherein said metal powders have a granulometry included between 20 and 70 μm.
10. Getter device according to claim 7, wherein the weight ratio between the Ca-Ba-Al alloy and the metal is included between 1:3 and 3:1.
11. Getter device according to claim 10, wherein said ratio is about 1:1.
12. Getter device according to claim 3 or 7, further containing a compound chosen among iron nitride, germanium nitride or mixtures thereof in a quantity up to 5% with respect to the total weight of the powders.
13. Getter device according to claim 3 or 7, wherein said packet of powders has a free surface having from two to eight radial depressions.
14. Getter device according to claim 3 or 7, wherein in said packet of powders there is a discontinuous metallic element, essentially parallel to the bottom of the container.

Fig. 1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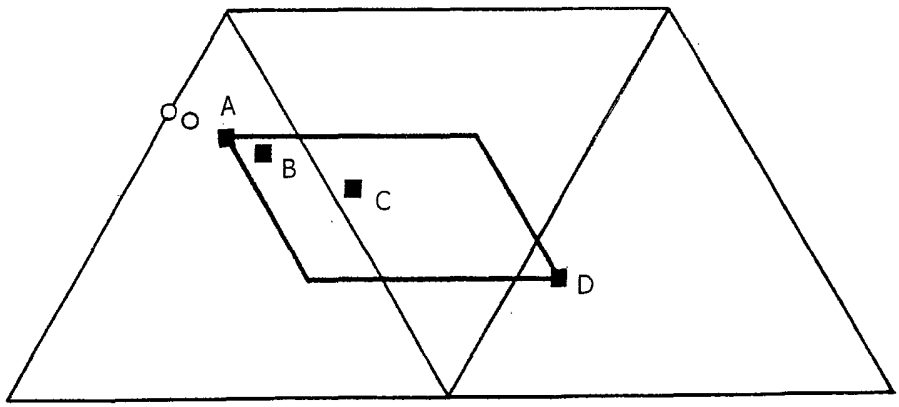
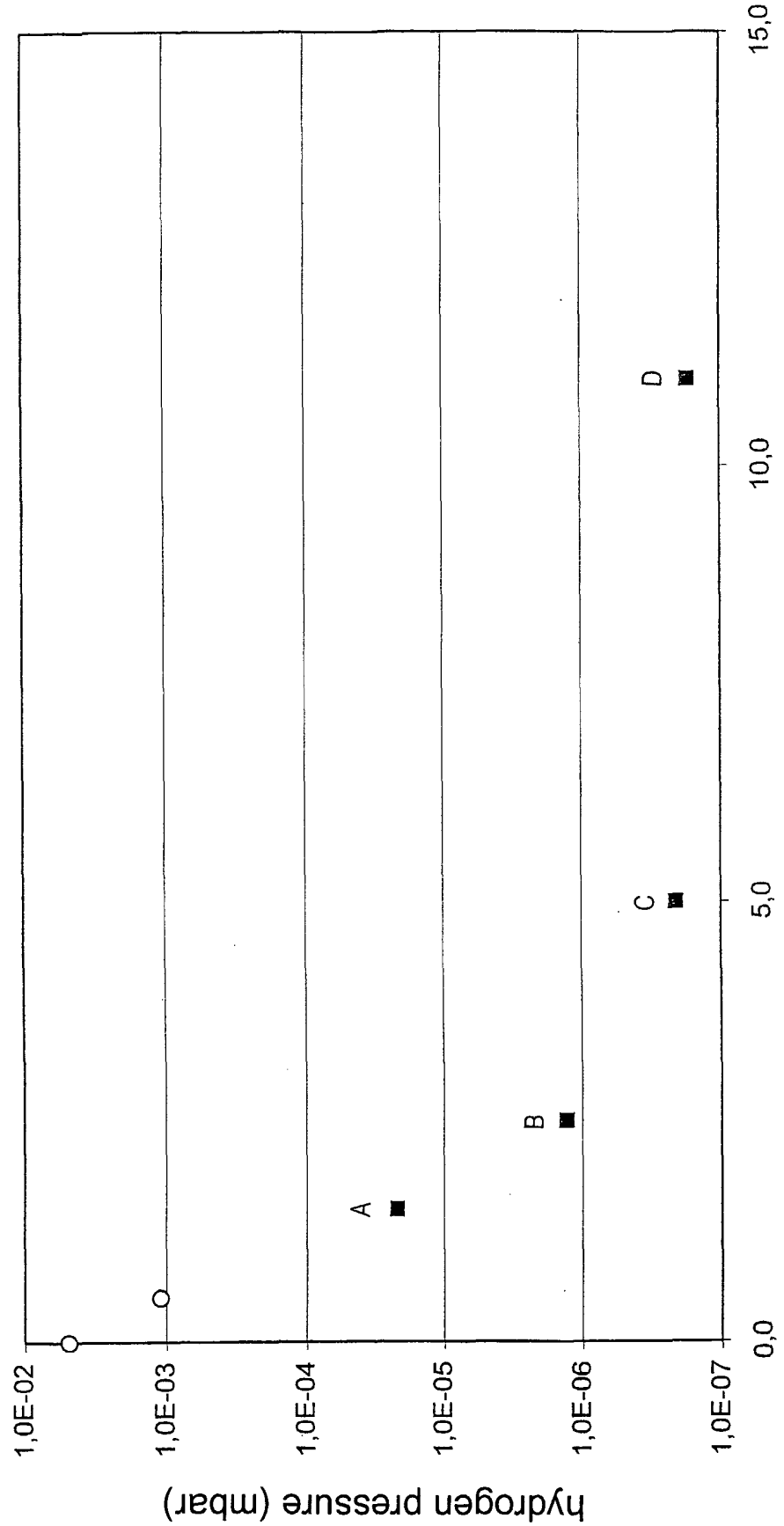

A
B
C
D

Fig. 1 a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1,0E-04
1,0E-05
1,0E-06
1,0E-07
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5,0
10,0
15,0
% barium by weight
A
B
C
D

Fig. 2

INTERNATIONAL SEARCH REPORT

Inte| ial Application No
PC1/1T 02/00676

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22C1/04 H01J7/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C22C H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	TURNBULL J C: "BARIUM, STRONTIUM, AND CALCIUM AS GETTERS IN ELECTRON TUBES" JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY, NEW YORK, NY, US, vol. 14, no. 1, December 1977 (1977-12), pages 636-639, XP000937555 ISSN: 0022-5355 abstract -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

'ormation on patent family members

Inte ıal Application No
PCI/IT 02/00676

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