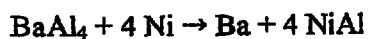


"GETTER DEVICES FOR CALCIUM EVAPORATION"

The present invention relates to getter devices for calcium evaporation within systems operating under vacuum, and particularly in cathode ray tubes (CRTs).

5 Getter devices based on the evaporation of a metal are known as evaporable getter devices. These devices have been used since the 50's for maintaining vacuum in cathode ray tubes of TV sets and, later, of computer screens; CRTs are also referred to in the field as kinescopes. The CRTs are evacuated during their manufacture by means of mechanical pumps and then hermetically sealed; however, vacuum in the tube tends
10 to decrease quickly, mainly due to the tube internal components outgassing. Therefore, a getter material, which can fix the gas molecules so as to preserve the vacuum level required for the working of the CRT, must be used inside the tube. The technological progress has indicated barium as such a getter material. Because of the high air reactivity of this metal, which renders troublesome all manufacturing operations, barium
15 is used in the form of the air stable compound $BaAl_4$. The compound is introduced in the CRT before the sealing thereof, and then is heated from the outside by means of radiofrequencies (RF) in order to accomplish barium evaporation; the thus evaporated barium condenses on the tube internal walls in the form of a film, which is the very getter element. Since barium evaporation requires temperatures of about $1200^{\circ}C$, the
20 powders of the compound are normally used in mixture with nickel powders; when the mixture temperature reaches about $850^{\circ}C$, the following exothermal reaction takes place:



25 The heat generated by the reaction increases the temperature of the system up to the temperature required for barium evaporation.

The use of barium as gettering element, and of $BaAl_4$ as the barium precursor, were defined more than fifty years ago, and they have been fundamental in the development of the manufacture of CRTs on a very large scale for use as screens.

However, the use of barium involves a few drawbacks.

30 First, like all heavy metals, it is a toxic element and therefore its use imposes particular precautions in all production steps of the compound $BaAl_4$, as well as in the

disposal of the CRTs at the end of their lives, in order to avoid ecological problems due to the element dispersion in the environment.

Further, inside CRTs barium is also present in portions which are hit by the high energy electron beams used for generating the image in the kinescope; in these conditions barium, and consequently the kinescope screen, emit X-rays which are known to be harmful for the health.

The article "Barium, strontium and calcium as getters in electron tubes" of J. C. Turnbull, published on the Journal of Vacuum Science and Technology, vol. 14, number 1, of January/February 1977, pages 636-639, considers the possibility of substituting barium with either strontium or calcium for the application in kinescopes. The precursors used in this study for the evaporation of strontium and calcium are obtained by melting of mixtures containing 40% of Sr and 60% of Al, and 35% of Ca and 65% of Al respectively (all percentages are by weight); the analyses of the obtained materials prove that in the first case the resulting material is a mixture of the compound SrAl_4 with free Al, and in the second case it is a complex mixture of phases, containing the compounds CaAl_2 , CaAl_4 and CaO without free Al. The results of the study are that, while in the case of strontium a film having gas sorption features comparable with those of barium can be obtained, calcium gives much inferior results; particularly, the study proves that with the same weight of metal, a strontium film has a sorption capacity (evaluated by oxygen tests) which is 75% of that of a barium film, whereas the capacity of a calcium film is only a quarter of that of the barium film. In confirmation of these results, US patent 3.952.226 still in the name of Turnbull describes, for barium substitution, the use of strontium-based evaporable getters, but it does not mention the possibility of employing similar calcium-based devices.

Furthermore, in addition to these theoretical evaluations, the whole world production of CRTs has been always based on the use of barium only as material of the getter film, and of its compound BaAl_4 as precursor of said film.

Object of the present invention is providing devices for the evaporation of calcium inside systems operating under vacuum, particularly cathode ray tubes.

These objects are achieved according to the present invention by means of getter devices for calcium evaporation comprising calcium-aluminum compounds containing

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about from 39% to 43% by weight (b.w.) of calcium. Preferably, getter devices of the invention comprise the compound CaAl_2 , that contains about 42.6% b.w. of calcium.

The invention will be described with reference to the drawings wherein:

- 5 - Figure 1 shows the features of metal evaporation by a first kind of evaporable getter devices of the invention and of the prior art;
- Figure 2 graphically shows a comparison between the velocity of gas sorption as a function of the sorbed quantity of a calcium film obtained by evaporation of a first kind of device of the invention and of a barium film obtained by evaporation of a prior art device, metal weight being equal.
- 10 - Figures 3 and 4 show the features of metal evaporation by another kind of evaporable getter devices of the invention.

Contrary to the results obtained with the Ca 35% - Al 65% b.w. compositions studied by Turnbull in the above discussed article, the inventors have discovered that by using calcium-aluminum compounds containing about from 39% to 43% by weight of calcium, it is possible to obtain calcium films having gas sorption features higher than those obtainable by barium films, having the same metal weight. Compositions containing more than about 43% b.w. calcium contain free calcium, and have proven to be rather unstable to air exposure, developing calcium oxide that may interfere with proper working of the getter devices; these compositions thus pose problems in the production, storing and shipping of calcium-based getter devices. On the other hand, compositions with less than about 39% calcium give rise when evaporated to a reduced yield of the element, without offering other advantages. Among the calcium-aluminum compounds of the invention, it is highly preferred the use of the pure compound CaAl_2 , that maximizes the calcium content without the above mentioned problems of instability to air. In the following, the description of the invention will be made with particular reference to the use of this compound.

Evaporable getter devices of the invention can be of the so-called "endothermal" type, containing only the compound CaAl_2 . These devices are so defined because all the heat required for barium evaporation must be supplied from the outside, normally through induction heating.

Alternatively, devices of the "exothermal" type can be used, wherein part of the

heat for calcium evaporation is provided by an exothermal reaction among CaAl_2 and a suitable further component of the device. The purposely added component can be nickel, as in the known barium-based devices; alternatively, as discovered by the inventors, in the case of calcium-based devices the use of titanium is possible.

5 The behaviour of exothermal devices using nickel is very different from that of devices where titanium is used.

10 The inventors have found with CaAl_2 -Ni mixtures surprisingly there is almost no dependence of the evaporated calcium quantity on the power supplied through radiofrequencies, even after the possible exposures to oxidizing gases at high temperatures that can take place during the CRT production steps. This behaviour seems to be linked to the high reactivity of these mixtures, that release almost all of the contained calcium as soon as the temperature for triggering the exothermal reaction is reached. This feature may greatly simplify the CRT production process, which requires less controls of induction heating parameters, such as power supplied to the induction
15 coil or total heating time. Calcium evaporation by these devices may however be rather violent, so it is preferred to use this mixture only in small dimensions getter devices.

20 CaAl_2 -Ti mixtures show a more usual behaviour, similar to the one known from barium-based getter devices, with the yield of calcium depending on the induction heating power (that influences the starting time of evaporation) and the total induction heating time.

 The use of devices containing both nickel and titanium is also possible, leading to an intermediate behaviour between the two described above.

25 Both endothermal and exothermal devices are formed of a container made of metal, generally steel. The container is upperly open and has generally the shape of a short cylinder (in the case of the smaller devices) or of an annular channel having a substantially rectangular cross-section. The container may have essentially the same shape as the containers used for the barium devices; some possible shapes of said devices are described in US patents Nos. 2.842.640, 2.907.451, 3.033.354, 3.225.911, 3.381.805, 3.719.433, 4.134.041, 4.504.765, 4.486.686, 4.642.516 and 4.961.040.

30 The compound CaAl_2 is simply prepared by melting of the two metal components in stoichiometric ratio. The melting can be made in an oven of any kind, for instance an

induction one, and is preferably made under inert atmosphere, for example under nitrogen.

The compound CaAl_2 is preferably used in the powder form, generally of particle size smaller than $500\text{ }\mu\text{m}$ and more preferably between 50 and $250\text{ }\mu\text{m}$.

5 In case of exothermal devices, the added metal, that can be either nickel or titanium or a mixture thereof, is preferably used in the form of powders having particle size lower than about $100\text{ }\mu\text{m}$ and more preferably comprised between about 20 and $70\text{ }\mu\text{m}$. With nickel or titanium in form of powders of particle size higher than $100\text{ }\mu\text{m}$, the contact with the grains of CaAl_2 is reduced, reducing the exothermal effect of the
10 mixture, while grain sizes lower than $20\text{ }\mu\text{m}$ make the powders more difficult to transport and, in the case of titanium, possibly pyrophoric.

 The weight ratio between CaAl_2 and the added metal can vary within broad limits. Particularly, when nickel is used, the weight ratio $\text{CaAl}_2\text{:Ni}$ can be comprised between about $20\text{:}80$ and $45\text{:}55$, and preferably between $38\text{:}62$ and $42\text{:}58$; when titanium is used,
15 the ratio $\text{CaAl}_2\text{:Ti}$ can be comprised between about $40\text{:}60$ and $75\text{:}25$, and preferably between $45\text{:}55$ and $50\text{:}50$. The use of higher amounts of CaAl_2 than indicated leads to too low amounts of added metal, and thus to only little heat generated by the exothermal reaction to help calcium evaporation; on the other hand, use of nickel or titanium in amounts greater than indicated leads to too little amounts of calcium releasable by the
20 devices.

 Also in the devices of the invention recourse can be had to the teachings of the prior art, relevant to the barium evaporable getters, in order to improve in some respects the performance thereof.

 For example, the device can contain percentages up to 5% by weight (of the
25 powder mixture) of a compound selected among nitrides of iron, germanium or mixed iron-germanium nitrides; in these devices nitrogen is released immediately before calcium evaporation, which allows a more diffuse metal film having a more homogeneous thickness to be obtained. Examples of nitrogenated devices for barium evaporation are given in US patents $3.389.288$ and $3.669.567$.

30 Both in case of exothermal and endothermal devices, the free surface of the powder packet in the container can have radial depressions (from two to eight, normally

four) in order to lessen heat transport in circumferential direction in the packet itself, thus reducing the problem of possible ejection of solid particles during Ca evaporation. For a more detailed illustration of the problem and of the solution provided by the radial depressions, reference is made to US patent 5.118.988.

5 Moreover, in order to improve homogeneity of the induction heating of the powder packet, a discontinuous metal element, essentially parallel to the container bottom, can be added in the packet itself as described in US patent 3.558.962 and in European patent application EP-A-853328.

10 Finally, in order to enhance protection of the devices against atmospheric gasses, mainly during the fritting operation referred to above, the whole packet of powders, or only some components of said packet, may be covered with a protecting film. Such layers are generally glassy and comprise boron oxide as the only or main component. Getter devices for evaporation of barium totally or partially protected by these films are described for instance in patent US 4,342,662 (disclosing getter devices wholly covered
15 by a thin film of a boron compound possibly containing silicon oxide up to 7% by weight) and in the published Japanese patent Hei-2-6185 (disclosing the protection of at least nickel by means of boron oxide only).

20 The invention will be further illustrated in the following examples. These non limiting examples illustrate some embodiments which are intended to teach those skilled in the art how to put the invention into practice and to represent the considered best way for carrying out the invention.

EXAMPLE 1

25 100 g of compound CaAl_2 are prepared by melting in a refractory crucible (mixed aluminum and magnesium oxides) 42,6 g of calcium shavings and 57,4 g of aluminum drops. The melting is made under nitrogen in an induction oven. After solidification of the melt, the ingot is ground and the powders are sieved, recovering the fraction having particle size lower than 210 μm . The X-rays diffractometry of the powders confirms that the material is CaAl_2 .

EXAMPLE 2

30 20 g of the CaAl_2 powder prepared as described in Example 1 are mixed with 80 g of nickel powder having average particle size of 40 μm . A set of devices for calcium

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evaporation is prepared with this mixture, using for each of them a steel container with an annular channel shape, having external diameter of 20 mm and channel width of 6 mm; each container is loaded with 1 g of mixture by compressing the powders with a shaped punch to which a pressure of about 6,500 kg/cm² is applied. The nominal calcium quantity in each device is 85 mg.

EXAMPLE 3

Five devices produced as described in example 2 are subjected to a calcium evaporation test. Each device is weighed and introduced into a glass flask wherein vacuum is made and inductively heated from outside by means of a coil positioned near the device. The total time (T.T.) for heating, that is the time during which power is applied through the coil, is 30 seconds in all tests. On the contrary the power is varied, so as to vary the triggering moment of the evaporation (defined as "Start Time", S.T., in the field): the higher is the power, the faster is the heating of the device and the sooner calcium evaporation starts. At the end of the evaporation process, the devices are taken out from the flask and weighed; from the weight difference between before and after evaporation, the quantity of evaporated calcium is determined. The results of the five tests, expressed as calcium yield as a function of the S.T., are given in Table 1 and graphically in Figure 1, wherein in ordinates the calcium yield is given, as percentage of evaporated metal with respect to the total calcium contained in the initial device, as a function of the S.T. value; the values obtained in the tests are indicated with circles, whereas line 1 represents the interpolation of these values with the least squares method.

Table 1

Start Time (seconds)	Evaporated Ca (milligrams)
12,1	48
14,4	51
15,2	50
16,5	55
16,6	52

EXAMPLE 4

Nine devices produces as described in example 2 are subjected to a calcium

evaporation test after having been exposed to air for one hour at a temperature of 450°C. This treatment simulates the conditions to which the devices are subjected during the CRTs manufacture operation called "fritting": in this operation the front and the back glass portion of the CRTs are sealed by melting a glass low melting paste.

- 5 During this treatment the getter devices are subjected to a partial oxidation which can involve problems of excessive exothermicity in the following evaporation operation. After the treatment at 450°C, the devices are subjected to the evaporation test according to the method described for example 3. The test results are given in Table 2 and graphically in Figure 1; in the graph, the values obtained in the tests are indicated with
 10 squares, whereas line 2 represents the interpolation thereof.

Table 2

Start Time (seconds)	Evaporated Ca (milligrams)
11,1	38
11,5	42
11,7	33
12,0	38
12,0	38
12,3	32
13,8	39
15,0	37
16,0	35

- In the graph in Figure 1 two curves relevant to the barium evaporation features from prior art devices are also given for comparison; curve 3 is relevant to evaporation
 15 of devices which were not subjected to the fritting treatment, whereas curve 4 is relevant to devices which were subjected to said treatment.

EXAMPLE 5

In this example the gas sorption features of calcium films produced starting from getter devices of the invention are evaluated.

- 20 A device produced as described in example 2 is introduced in a measuring chamber having an internal volume of 8,35 liters. The chamber is evacuated and

subjected to a degassing treatment of the walls at 150°C for 16 hours under pumping with a turbomolecular pump. At the end of the treatment pumping is stopped and calcium is evaporated with a T.T. of 30 seconds. The gas sorption test is then started, by using carbon monoxide CO as the test gas. Subsequent amounts of CO are introduced in the chamber; every amount being such that the pressure in chamber is brought to a value of $8,8 \times 10^{-3}$ mbar. By means of a capacitive manometer the pressure decrease in the measuring chamber, due to sorption of CO by the calcium film, is measured. When the pressure in the chamber has reached the value of about $1,33 \times 10^{-4}$ mbar, the next CO amount is introduced. The results of this sorption test are graphically given in Figure 2, which shows the sorption velocity per gram of the calcium film, S, as a function of the CO quantity sorbed per gram of film, Q. The graph in figure 2 is built by measuring the average CO sorption velocity during the first 4 seconds after every gas addition, and by reporting this value as a function of the total CO quantity supplied to the sample during the various dosages; S is measured as a gas quantity (in millibar per liter, mbar x l) divided by the test time (in seconds, s) and by the weight of the calcium film (in grams, g); Q is measured as the gas quantity in millibars per liter divided by the weight of the calcium film in grams. The sorption capacity of the film is considered to be exhausted when the initial pumping velocity is reduced to 1% of the initial one. At the end of the test the total sorption capacity of the calcium film is calculated.

This test is repeated for a confirmation of the reproducibility of the obtained data; the results of the two tests are summarized in Table 3.

EXAMPLE 6 (COMPARATIVE)

The test of example 5 is repeated on a production barium getter device, comprising 570 mg of a mixture formed of 47% of a BaAl₄ compound and 53% of Ni, for a nominal content of Ba of 150 mg. The test results are given in Figure 2 as curve 6. The test is repeated in order to check the reproducibility thereof; the results of these two tests are summarized in Table 3, wherein the compound used for evaporation of the alkaline-earth metal, the grams of the evaporated metal, the total quantity of sorbed CO and the specific film capacity (capacity per unit of weight of the film metal) are indicated.

Table 3

Compound	Metal yield (g)	Total sorbed CO (mbar x l)	Total capacity (mbar x l / g)
CaAl ₂	0,040	0,31	7,7
CaAl ₂	0,042	0,30	7,1
BaAl ₄	0,093	0,55	5,9
BaAl ₄	0,123	0,63	5,1

EXAMPLE 7

45 g of the CaAl₂ powder prepared as described in Example 1 are mixed with 55 g
5 of titanium powder having average particle size of 30 μ m. A set of devices for calcium
evaporation is prepared with this mixture, using for each of them a steel container with
an annular channel shape, having external diameter of 20 mm and channel width of 6
mm, and filling each device with 500 mg of the CaAl₂-Ti mixture compressed in the
container by applying to the punch a pressure of about 18,000 kg/cm². The nominal
10 loading of calcium in each device is 96 mg.

EXAMPLE 8

The test of Example 3 is repeated on a series of samples prepared as described in
Example 7. The T.T. value is 30 seconds in each test. The results of these tests are given
in the graph in figure 3.

EXAMPLE 9

The test of Example 8 is repeated on a series of samples that, after preparation, are
subjected to a heat treatment in air at 450 °C for 1 hour, simulating the "fritting"
conditions that the devices may undergo in the CRT production lines. The results of
these tests are given in the graph in figure 4.

20 The results given in Figure 2 and Table 3 prove that in spite of what was believed
before it is possible, by operating with the devices of the invention, to obtain calcium
films having a gas sorption capacity per unit of metal weight comparable and even
slightly higher, than that of the barium film obtained with the known devices.

25 Figure 1 further shows the metal yield by exothermal CaAl₂-Ni getter devices of
the invention and of prior art Ba-based getter devices as a function of S.T., T.T. being

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equal, both in the case of devices subjected to the fritting treatment and of devices not subjected to said treatment. From the comparison of the metal yield curves in Figure 1 it may be deduced that:

- 5 - differently from the barium devices of the prior art, the invention devices using nickel as added metal have a metal yield which is essentially independent from the evaporation Start Time, and therefore from the power applied through the induction coil, with the possibility of employing lower powers;
- 10 - the calcium yield of devices of the invention is essentially independent from the S.T. even after fritting.

By virtue of these two features, the power supplied through the coil can be reduced with $\text{CaAl}_2\text{-Ni}$ devices, and also a lower control of the evaporation parameters is necessary: in fact, whereas in the barium devices variations of S.T. or T.T. (for example due to errors in the control of these parameters in the CTRs manufacture
15 process) bring to considerable differences in the quantity of evaporated barium and therefore to different film sorption features, with the devices of the invention similar variations of S.T. or T.T. have practically no influence on the metal yield.

Finally, figures 3 and 4 show that $\text{CaAl}_2\text{-Ti}$ too have good calcium-releasing properties, with a yield that is over 80% of the nominal calcium content (96 mg) at high
20 applied powers (lower S.T. values) with non-fritted devices, and over 75% with fritted devices.

CLAIMS

1. Getter device for calcium evaporation comprising a calcium-aluminum compound containing about from 39% to 43% by weight of calcium.
2. Getter device according to claim 1 wherein the calcium-aluminum compound is CaAl_2 .
3. Getter device according to claim 1 formed of an upperly open metal container having the shape of a short cylinder or of an annular channel with substantially rectangular cross-section.
4. Getter device according to claim 3, wherein the calcium-aluminum compound is in the powder form.
5. Getter device according to claim 4, wherein the powders of the calcium-aluminum compound have particle size lower than about 500 μm .
6. Getter device according to claim 5, wherein the particle size of the powders of the calcium-aluminum compound is between about 50 and 250 μm .
7. Getter device according to claim 4, inside which only the calcium-aluminum compound is provided.
8. Getter device according to claim 4, inside which the calcium-aluminum compound is mixed with nickel.
9. Getter device according to claim 8, wherein nickel is in the powder form and the $\text{CaAl}_2\text{-Ni}$ mixture forms a packet of powders.
10. Getter device according to claim 9, wherein the nickel particle size is lower than about 100 μm .
11. Getter device according to claim 10, wherein the nickel particle size is between about 20 and 70 μm .
12. Getter device according to claim 8, wherein the weight ratio between the calcium-aluminum compound and nickel is between 20:80 and 45:55.
13. Getter device according to claim 12, wherein the weight ratio between the calcium-aluminum compound and nickel is between about 38:62 and 42:58.
14. Getter device according to claim 8, comprising up to about 4% by weight of a compound selected among the nitrides of iron, germanium or mixed.
15. Getter device according to claim 9, wherein the free surface of the powder packet



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in the container has two to eight radial depressions.

16. Getter device according to claim 9, wherein in the powder packet is present a discontinuous metal element, essentially parallel to the container bottom.
17. Getter device according to claim 9, wherein at least one of the powders is covered
5 with a boron-based protecting film.
18. Getter device according to claim 4, inside which the calcium-aluminum compound is mixed with titanium.
19. Getter device according to claim 18, wherein titanium is in the powder form and the CaAl_2 -Ti mixture forms a packet of powders.
- 10 20. Getter device according to claim 19, wherein the titanium particle size is lower than about 100 μm .
21. Getter device according to claim 20, wherein the titanium particle size is between about 20 and 70 μm .
22. Getter device according to claim 18, wherein the weight ratio between the
15 calcium-aluminum compound and titanium is between 40:60 and 75:25.
23. Getter device according to claim 22, wherein the weight ratio between the calcium-aluminum compound and titanium is between about 45:55 and 50:50.
24. Getter device according to claim 18, comprising up to about 4% by weight of a compound selected among the nitrides of iron, germanium or mixed.
- 20 25. Getter device according to claim 19, wherein the free surface of the powder packet in the container has two to eight radial depressions.
26. Getter device according to claim 19, wherein in the powder packet is present a discontinuous metal element, essentially parallel to the container bottom.
27. Getter device according to claim 19, wherein at least one of the powder
25 components is covered with a boron-based protecting film.

