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(54) Evaporable getter device with reduced time of activation

(57) An evaporable getter device is described adapted for the use in traditional television tubes or flat displays with reduced barium evaporation time. The device comprises, in addition to powders of $BaAl_4$ alloy and nickel used in the known getter devices, powder of a third component selected from iron, aluminum, titanium or their alloys.

EP 0 858 093 A1

Description

The present invention concerns an evaporable getter device with reduced activation time.

As is known, the evaporable getter materials are mainly employed for the maintenance of vacuum at the inside of picture tubes for television sets and of computer screens. The use of evaporable getter materials at the inside of flat displays, being at present in a developing stage, is also under study.

The getter material being commonly used in picture tubes is metallic barium which is deposited in the form of a thin film on an inner wall of the tube. To obtain such a film use is made of devices, known in the field as evaporable getter devices, which, are introduced in the tube during its manufacturing. These devices are formed of an open metallic container comprising therein powders of a compound of barium and aluminum, $BaAl_4$, generally having a particle size of less than about 250 μm, and powders of nickel, generally with a particle size of less than 60 μm, in a ratio by weight of about 1:1. These devices are well known in the technique; reference is made in this respect for example to US patent 5.118.988 in the applicant's name. Barium is caused to evaporate by induction heating the device by means of a coil at the outside of the picture tube itself, in an activation process also defined as "flash"; when the temperature of the powders reaches a value in the range between about 800 and 850°C, the following reaction takes place:

$$BaAl_4 + 4\ Ni \rightarrow Ba + 4\ NiAl \qquad (I)$$

This reaction is strongly exothermic and raises the temperature of the powders to about 1200°C, at which barium is evaporated and deposited onto the walls of the tube thus forming the metallic film.

The time required to evaporate all the barium contained in the device, being measured starting from the moment at which the device begins being supplied with power by means of the coil, is defined in the field with the term "total time", which will be used in the following portion of the description and in the claims also an its abridged form TT. For example, to obtain barium films of about 300 mg as required by colour picture tubes of big size, the required TT with the present getter devices is of 40-45 seconds. However this time corresponds to the slow step in the present lines for manufacturing electronic tubes, whereby it is a requirement of the manufacturers to have devices which can release barium with lower TT values.

To obtain such a result, in principle the power supplied by the coil can be increased or an increase of the powders reactivity can be obtained by reducing their particle size.

However with the available getter devices an increase of the coil power is impossible. In fact, by doing so, the container of the powders raises its temperature too quickly and there is not time enough for a homogeneous diffusion in the packet ofpowders of heat, thus giving rise to the container melting.

Also a reduction of the particle size of the powders is impossible, as this would bring to an excessive and local increase of the reaction speed between $BaAl_4$ and Ni with consequent bulging of the packet of powders and possible ejection of pieces from the latter.

Object of the present invention is that of providing an evaporable getter device with reduced activation time that does not show the inconveniences of the prior art.

Such an object is obtained according to the present invention with an evaporable getter device having a reduced activation time comprising a metallic container in which a mixture is present including:

- powder of $BaAl_4$ compound;
- powder of nickel; and
- powder of a third component chosen among aluminum, iron, titanium and their alloys in a quantity range between about 0,3% and about 5% of the total weight of the mixture.

The quantity of powder of the third component in the mixture of powders depends on the actually employed component and generally is in the range between about 0,3% and 5%. In particular, the percentage of the third component is preferably comprised between about 0,8% and 2% in case of aluminum, between about 0,3% and 1,2% in case of iron and between about 0,5% and 5% in case of titanium. With quantities of the third component being lower than those indicated the desired effect of reducing the barium evaporation time is not obtained. On the contrary, when operating with quantities of the third component being higher than those above indicated, the barium flash becomes of raging nature and hardly controllable. The ratio by weight between nickel and $BaAl_4$ is the same as in the prior art devices, generally of about 1:1; in particular, in this field getter devices are broadly employed having a ratio of 5.3:4.7 between nickel and $BaAl_4$.

For the purposes of the invention the third component is not required to be of particularly high purity and use can be made of powders of commercial metals or alloys, generally having a purity of about 98-99%. The particle size of

the powdered third component being useful for the purposes of the invention is less than about 80 μm and preferably less than about 55 μm.

The powders of nickel and of the compound $BaAl_4$ which are employed in the getter devices of the invention are the same as those used in the prior art devices; generally powders with particle size of less than about 60 μm are used for nickel, while for the compound $BaAl_4$ powders having a particle size of less than about 250 μm are generally employed.

The metallic container can be made from various materials, such as nickel-plated iron or constantan; preferred is the use of steels AISI 304 or AISI 305 which show a good resistance to oxidation and thermal treatment as well as a good cold workability. The metallic container can have any shape and in particular whichever one of the shapes known and used in the field, such as those of the devices according to the US Patents 4,127,361 - 4,323,818 - 4,486,686 - 4,504,765 - 4,642,516 - 4,961,040 and 5,118,988.

Particularly interesting is the possibility of obtaining evaporable getter devices with a reduced time of activation which are also frittable; with this term getter devices are meant which can withstand to an oxidizing atmosphere at a temperature of about 450°C for a duration time of up to 2 hours; these being the conditions which such devices have to undergo in some processes for manufacturing picture tubes. During the barium evaporation from frittable getter devices a greater heat quantity is generated than in the common getter devices, with consequent higher difficulties in keeping the packet of powders in the container. Frittable getter devices with a quantity of evaporable barium up to about 200 mg have been manufactured and sold by the applicant since several years. On the contrary frit sealable getter devices which can evaporate greater quantities of barium and in particular of about 300 mg require that particular solutions are adopted to take into account their greater reactivity; the patent application with the title "FRITTABLE EVAPORABLE GETTER DEVICE HAVING A HIGH YIELD OF BARIUM" in the applicant's name and having the same filing date of the present application, discloses the manufacturing of frittable getter devices obtained through the addition of elements retarding the heat dispersion in a circumferential direction in the packet of powders and the addition of a discontinuous metallic element, essentially flat, in the same packet. By adding a third component to frittable getter devices either of the traditional type or of the high yield type it is possible to obtain frittable getter devices with comparable characteristics of barium emission, but during a reduced evaporation time.

The invention will be further illustrated by means of the following examples. These non-limiting examples show some embodiments designed to teach those skilled in the art how to practice the invention and to represent the best considered mode for putting into practice the invention.

EXAMPLE 1

A number of getter devices all equal to each other is prepared by using for each of them a container made of steel AISI 304 having diameter of 20 mm and height of 4 mm with the bottom shaped with elevations 1 mm high as described in US Patent 5,118,988 cited herein. For each sample a homogeneous mixture is poured into the container, being comprised of 767 mg of powdered BaAl4 having a particle size of less than 250 μm, 866 mg of powdered nickel having a particle size of less than 60 μm and 18 mg of powdered iron with a 99% purity having a particle size of less than 80 μm. The mixture of powders is then compressed at the inside of the container by a proper punch. The samples are tested by placing them one at a time into a measuring chamber made of glass, connected to a pumping system, evacuating the chamber and carrying out a barium evaporation test by following the method described in the standard ASTM F 111-72; every device is heated by means of radio frequencies with such a power that the evaporation starts 12 s after the heating has begun; the tests are different from one another as to the heating Total Time, which is caused to vary in the various tests in a range between 35 and 45 s. At the end of each test the evaporated barium quantity is detected. The TT required for evaporating from the device a barium quantity of 300 mg is reported in Table 1.

EXAMPLE 2

A number of getter devices all identical to each other is prepared by using for them a steel container as described in Example 1. Within this container there is positioned a net of steel AISI 304 with meshes of 1,5 mm width, resting on the bottom elevations. For each sample a homogeneous mixture is poured into the container, being comprised of 767 mg of powdered $BaAl_4$ having a particle size of less than 250 μm, 866 mg of powdered nickel having a particle size of less than 60 μm and 18 mg of powdered aluminum, of 99% purity and having a particle size of less than 50 μm. The mixture of powders is then compressed at the inside of the container with a punch so shaped as to form at the packet surface four radial recesses. The samples thus obtained are treated at 450°C during 1 hour in air to simulate the frit sealing conditions. A barium evaporation test is then carried out on every sample like according to Example 1. Also in this case each device is heated by means of radio frequencies with such a power that the evaporation starts 12 s after the heating has begun, while the heating is maintained during a TT that is different from sample to sample and varying in a range between 35 and 45 s, then detecting the TT value required to evaporate from the devices a barium quantity

of 300 mg.

The results of the test are reported in Table 1.

(COMPARATIVE) EXAMPLE 3

The test of example 1 is repeated with a series of samples identical to those of example 1, but without powdered iron, by heating the devices with radio frequencies at a power level such that the evaporation starts 12 s after the heating has started and using different TT, variable between 35 and 45 s. The required TT for evaporating 300 mg of barium from these samples is reported in Table 1.

(COMPARATIVE) EXAMPLE 4

The series of tests of example 2 is repeated by using getter devices identical to those of Example 1 but without powdered aluminum. The required TT to evaporate 300 mg of barium from these samples is reported in Table 1.

EXAMPLE	% THIRD COMP.	TOTAL TIME (s)
1	1,09 (Fe)	35
2	1,09 (Al)	35
3	0	45
4	0	40

As it is appreciated from the results in the Table, with the devices according to the invention it is possible to obtain a yield of 300 mg of barium with TT of 35 s, while obtaining the same yield with samples of the prior art takes times 5 or 10 s longer.

Claims

1. Evaporable getter device with reduced activation time, comprising a metallic container with a mixture therein comprising:

   - powder of $BaAl_4$ compound;
   - powder of nickel; and
   - powder of a third component chosen among aluminum, iron, titanium and their alloys in a quantity comprised between about 0,3% and about 5% of the total weight of the mixture.

2. An evaporable getter device according to claim 1, wherein when the third component is aluminum its percentage by weight in the mixture is comprised between about 0,8% and about 2%.

3. An evaporable getter device according to claim 1, wherein when the third component is iron its percentage by weight in the mixture is comprised between about 0,3% and about 1,2%.

4. An evaporable getter device according to claim 1, wherein when the third component is titanium its percentage by weight in the mixture is comprised between about 0,5% and about 5%.

5. A device according to claim 1, wherein the ratio by weight between nickel and $BaAl_4$ is about 1:1.

6. A device according to claim 1, wherein the ratio by weight between nickel and $BaAl_4$ is 5,3:4,7.

7. A device according to claim 1, wherein the powder of the third component has a particle size of less than about 80 μm.

8. A device according to claim 7, wherein the powder of the third component has a particle size of less than about

55 μm.

9. A device according to claim 1, wherein the powder of nickel has a particle size of less than about 60 μm.

10. A device according to claim 1, wherein the powder of $BaAl_4$ has a particle size of less than 250 μm.

11. An evaporable getter device with reduced activation time and being frittable, comprising:

- an upperly open metallic container;
- a mixture of powders in the container, in the form of a packet on the upper surface of which there are formed radial recesses, wherein the mixture comprises powders of $BaAl_4$, nickel and a third component chosen from aluminum, iron, titanium and their alloys, and wherein the third component is present in a quantity between about 0,3% and about 5% of the total weight of the mixture;
- a discontinuous metallic element of essentially flat shape and essentially parallel to the bottom of the container, being immersed in the packet of powders at a position spaced apart from the bottom of the container, such as not to emerge at the free surface of the packet itself.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 83 0001

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 Y	US 4 128 782 A (FRANSEN JAN J B ET AL) * column 2, line 3 - line 16 *	1,4,5 9-11	H01J7/18 H01J29/94
Y	PATENT ABSTRACTS OF JAPAN vol. 015, no. 250 (E-1082), 26 June 1991 & JP 03 078928 A (TOSHIBA CORP), 4 April 1991, * abstract *	9	
Y	US 4 717 500 A (FISCH HERBERT A ET AL) * column 2, line 31 - line 51 *	10	
Y	WO 89 10627 A (GETTERS SPA) * figures * * page 8, paragraph 2 *	11	
A	US 5 508 586 A (MARTELLI DANIELE ET AL) * example 1 *	1	
D,A	WO 91 06113 A (GETTERS SPA) * example 1 *	1,11	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	7 April 1998	Colvin, G

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

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