United States Patent [19]

della Porta et al.

[11] **3,768,884**

[45] **Oct. 30, 1973**

[54] **GETTERING**

[75] Inventors: **Paolo della Porta; Elio Rabusin,** both of Milan, Italy

[73] Assignee: **S.A.E.S. Getters S.p.A.,** Milan, Italy

[22] Filed: **Feb. 1, 1972**

[21] Appl. No.: **222,510**

Related U.S. Application Data

[62] Division of Ser. No. 34,319, May 4, 1970, Pat. No. 3,669,567.

[52] **U.S. Cl.** **316/25**

[51] **Int. Cl.** **H01j 9/38**

[58] **Field of Search** 316/25; 313/174, 313/176, 181; 417/48

[56] **References Cited**

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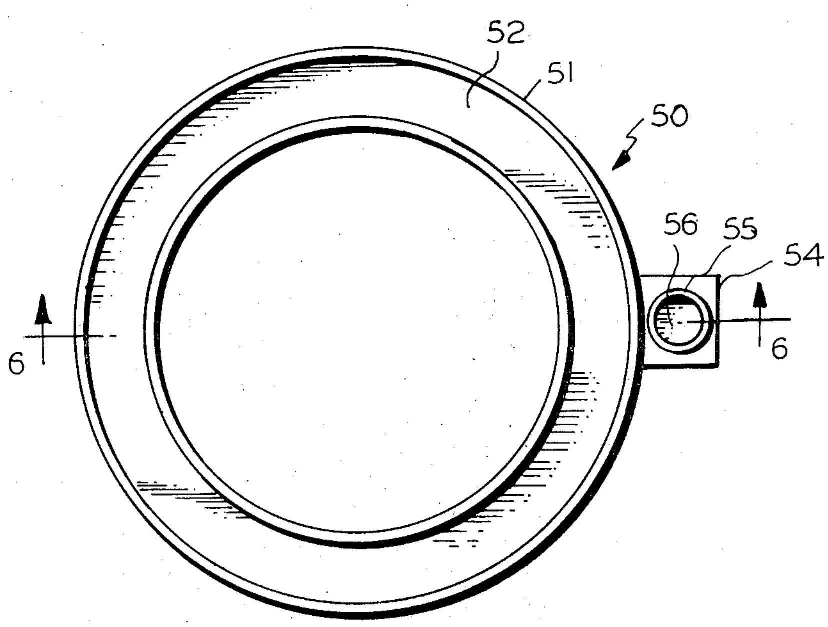
3,389,288	6/1968	Porta et al.	313/174
3,387,908	6/1968	Fogelson	316/25
3,388,955	6/1968	Porta et al.	316/25

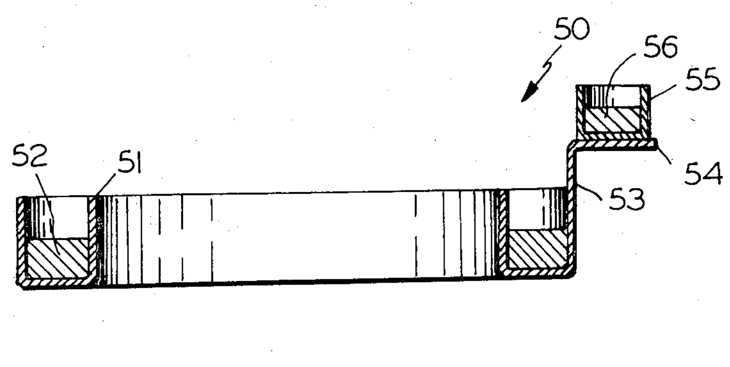
Primary Examiner—Charles W. Lanham
Assistant Examiner—J. W. Davie
Attorney—David R. Murphy et al.

[57] **ABSTRACT**

A getter device comprising an evaporable getter metal and first and second sources of gas; means for releasing the gas from the first source prior to and preferably also during evaporation of the getter metal; and means for releasing the gas from the second source during the latter part of the period of getter metal evaporation.

10 Claims, 12 Drawing Figures





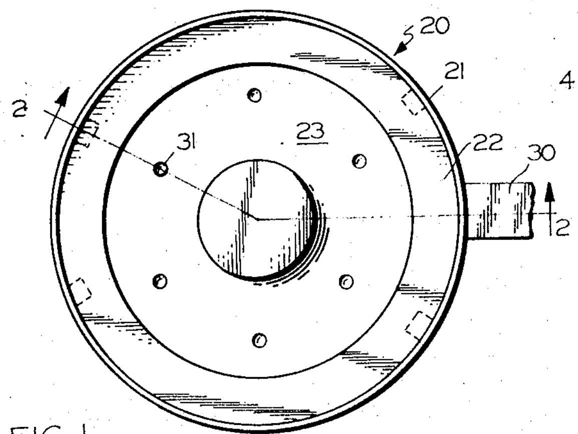


FIG.1

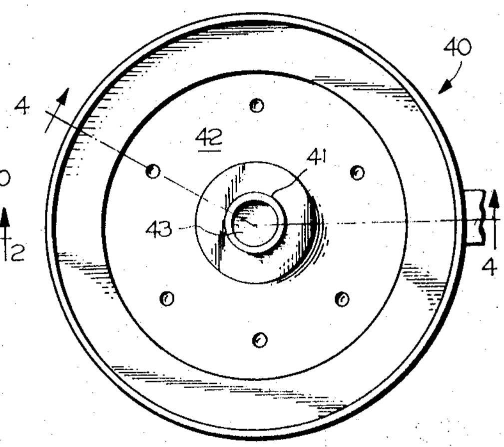


FIG.3

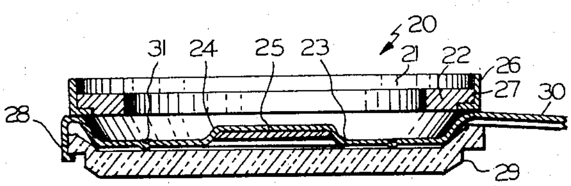


FIG.2

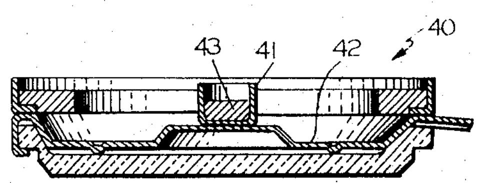


FIG.4

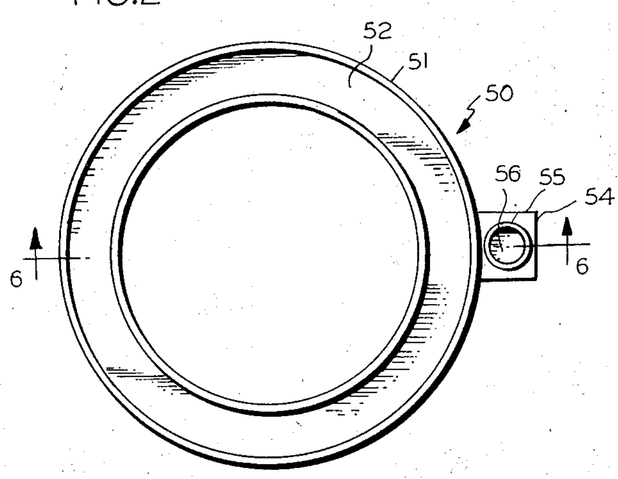


FIG.5

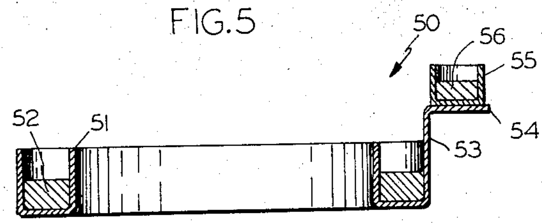


FIG.6

Patented Oct. 30, 1973 3,768,884

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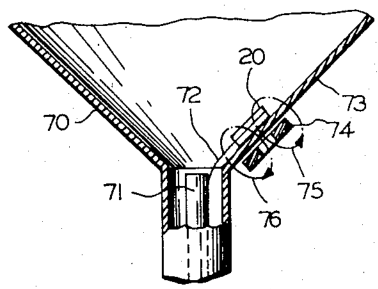

FIG.8

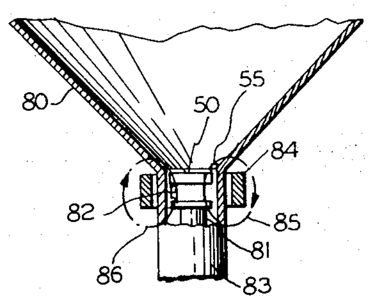

FIG.9

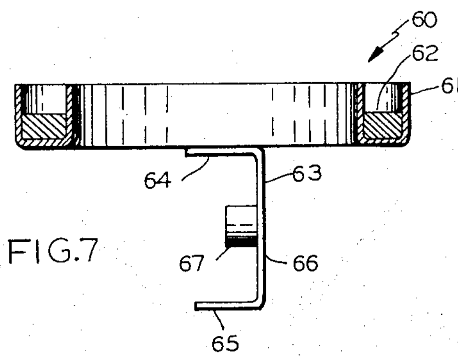

FIG.7

Patented Oct. 30, 1973 3,768,884

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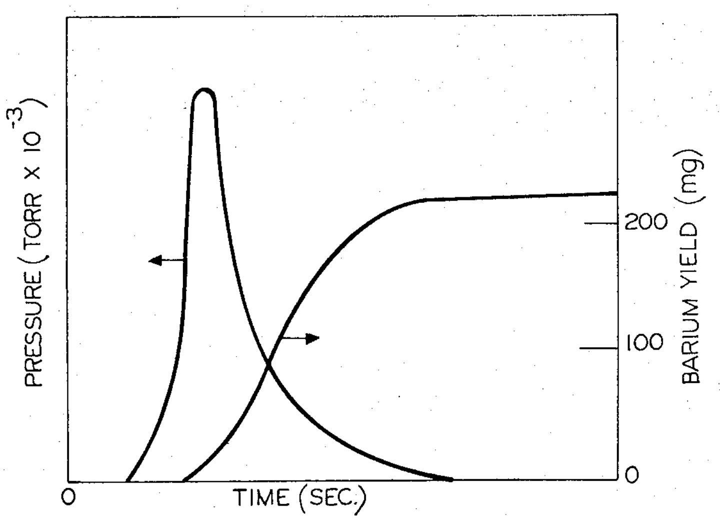
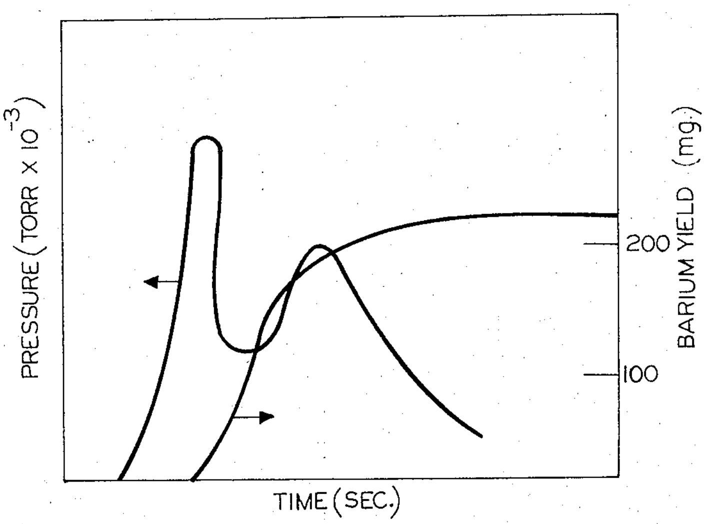


FIG. 10

FIG. 11



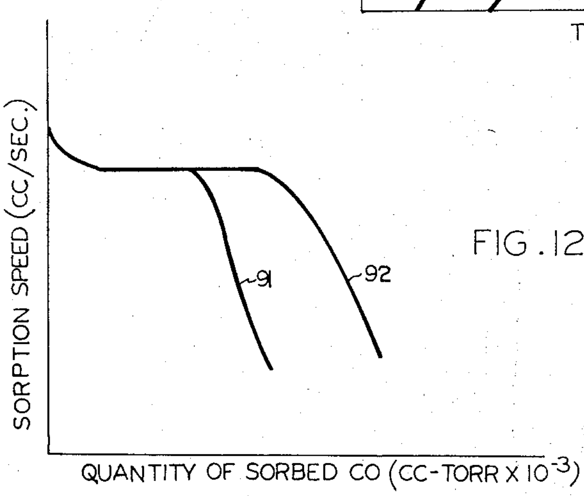


FIG. 12

GETTERING

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a divisional of U.S. application Ser. No. 34,319 filed May 4, 1970, now U.S. Pat. No. 3,669,567.

Getter devices which release an evaporable getter metal such as barium in a vacuum are well-known. The getter metal released by these devices deposits as a film on the inside walls of the vacuum vessel. These devices are commonly employed in electronic tubes in general and in cathode-ray tubes such as television tubes in particular.

Getter devices as described in U.S. Pat. Nos. 3,388,955 and 3,389,288 have recently been introduced and have found wide acceptance for use in electronic tubes. These getter devices are constructed such that the getter metal, prefereably barium, is evaporated in the tube in the presence of a gas. By virtue of the presence of this gas the getter metal is distributed preferentially on the conical walls rather than the screen portion of the cathode-ray tube. Unfortunately, the total sorptive capacity of the getter metal film produced by such devices is less than desired. It is well-known in the art that the sorptive capacity of barium films can be increased by evaporating barium in the presence of a gas to form the film (See British Specification 496,856). However, greatly increasing the amount of gas can result in an undesirable decrease of the sorptive capacity of the film.

Naturally increasing the quantity of the getter metal will increase the total quantity of gas which can be sorbed within the vessel. However, an increased quantity of getter metal tends to deposit itself on the screen portion of the cathode ray tube causing a number of problems. Firstly in the case of television tubes wherein the screen portion has no shadow mask, such as black and white television tubes, the getter metal film inhibits the passage of electrons and decreases the brightness of the picture.

In tubes having an aluminum coating over the phosphors any barium in contact with the aluminum can adversely affect the aluminum. During the operation oxygen evolved in the tube sorbed by the barium and is converted to barium hydroxide in the presence of water. This barium hydroxide attacks the aluminum damaging it.

Color television tubes are conventionally provided with a shadow mask designed to stop those electrons which are not directed to one of the three primary color phosphors. A barium film deposited on the shadow mask can cause uneven absorption of electrons and consequent uneven heating of the shadow mask. This uneven heating can warp the shadow mask causing misalignment of the holes in the mask with the primary color phosphors. This misalignment in turn causes untrue colors in the picture.

Electrons striking the barium film on the screen portion of the tube can cause sorbed gases to be re-evolved from the film. This effect is especially acute when the electrons have a high speed such as that encountered in color television tubes where the voltage between the electron guns and the screen is on the order of 25 kilovolts. This effect is present although somewhat less serious in black and white television tubes where this voltage is typically 10 to 15 kilovolts.

Thus it can be seen that simply increasing the amount of getter metal in a television tube is not a practical way to increase the gas sorptive capacity of the getter metal in the tube.

It is therefore an object of the present invention to provide novel getter devices which are substantially free of the disadvantages of one or more prior devices.

Another object is to provide getter devices having an increased sorptive capacity.

A further object is to provide getter devices which produce films having an increased sorptive speed.

A still further object is to provide a novel process of depositing a getter metal film on the inside walls of vessels in general and cathode-ray tubes in particular.

Yet another object is to provide getter devices comprising a getter metal and a gas-releasing material for use in cathode-ray tubes which produce a getter metal film of desirable distribution having a higher sorptive capacity than those of prior devices.

Additional objects and advantages of the present invention will be apparent by reference to the following detailed description and drawings wherein:

FIG. **1** is a plan view of the getter device of the present invention;

FIG. **2** is a sectional view taken along line **2—2** of FIG. **1**;

FIG. **3** is a plan view of a modified getter device of the present invention;

FIG. **4** is a sectional view taken along line **4—4** of FIG. **3**;

FIG. **5** is a plan view of yet another modified getter device of the present invention;

FIG. **6** is a sectional view taken along line **6—6** of FIG. **5**;

FIG. **7** is a sectional view of still another modified getter device of the present invention similar to that of FIGS. **5** and **6**;

FIG. **8** is a partial sectional view of a cathode-ray tube employing a getter device of the present invention;

FIG. **9** is a partial sectional view of a cathode-ray tube employing a modified form of the getter device of the present invention;

FIG. **10** is a graph indicating the pressure in a cathode-ray tube and the barium yield as a function of time characteristic of a prior getter device;

FIG. **11** is a graph similar to that of FIG. **10** but showing the characteristics of the getter devices of the present invention;

FIG. **12** is a graph showing the sorption speed as a function of the quantity of carbon monoxide sorbed for a getter device of the present invention compared to a certain control getter device;

According to the present invention there is provided a getter device comprising an evaporable getter metal and first and second sources of gas; means for releasing the gas from the first source prior to and preferably also during evaporation of the getter metal; and means for releasing the gas from the second source during the latter part of the period of getter metal evaporation. Such devices produce getter metal film having increased sorptive speeds and sorptive capacity.

The preferred devices are those which comprise a ring of an inductively heatable material, a mixture of a first gas-releasing material and an evaporable getter material in thermal proximity to the ring, and a second gas-releasing material adapted to release its gas during the latter period of getter metal evaporation.

Any evaporable getter metal can be employed in the devices of the present invention such as the alkali or alkaline earth metals, examples of which include among others calcium, magnesium, strontium, and barium. Barium is the preferred getter metal because of its well-known sorptive characteristics. The getter metal can be employed alone but is preferably employed in the form of a getter alloy comprising the getter metal and one or more less-reactive metals. Such alloys are less reactive towards air and are easier to handle. The preferred getter alloys are those of barium and aluminum, generally in weight ratio of about 10:5 to 10:20, and especially binary alloys containing about 50 to 56 percent barium, balance aluminum. The getter metals and getter alloys can be employed alone or in admixture with other substances. When employed alone so-called endothermic getter devices are produced. These devices rely upon induction heating in order to provide the heat of vaporization of the getter metal. More preferably the getter alloy is employed admixed with nickel to create an exothermic getter device wherein a portion of the heat of vaporization of the getter metal is supplied by an exothermic reaction between the nickel and the barium-aluminum alloy.

the ring of inductively heatable material can have a wide variety of geometric shapes provided that it is continuous. In one preferred embodiment of the present invention, the ring is annular in shape whereas in another embodiment especially useful with exothermic getter materials the ring comprises a vertically extending wall attached to a short horizontal wall.

In the broadest aspect any material which releases a gas is suitable for use as the gas-releasing material in the present invention. However, the preferred gas-releasing materials are those which are stable to temperatures up to 400° C in order that they can be concurrently heated with other parts of the device and/or the tube in order to facilitate de-gasing. Other preferred gas-releasing materials are those which are stable in air, by which is meant, those which neither decompose nor pick up undesirably large quantities of gas from the atmosphere.

The gas-releasing material can be selected such that virtually any gas is released under the desired conditions. However, the preferred gases are the active gases. An active gas is one which is sorbed by the employed getter metal. Examples of suitable gases include among others; carbon monoxide, carbon dioxide, oxygen, hydrogen, and nitrogen. The preferred gases are hydrogen and nitrogen, hydrogen because of its well-known incidental benefit to cathode activity, and nitrogen because of the rate at which it is sorbed by the preferred getter metals and because of its relatively high mass permitting a relatively small amount to be employed to effectively control getter film distribution. Nitrogen is most preferred.

Examples of suitable gas-releasing materials include among others: barium carbonate, the metallic hydrides, and nitrides such as barium nitride, barium hydride, titanium hydride, phosphorous nitride, and most preferably iron nitride (Fe_4N). Iron nitride is preferred because of its stability in air and its decomposition temperature which is above that commonly employed in de-gasing and is below that of barium evaporation. Furthermore, it yields nitrogen, the preferred gas.

Although the gas-releasing materials can be combined with the device in any suitable manner in one preferred embodiment of the present invention, the first gas-releasing material is admixed with the evaporative getter metal, and this mixture positioned in the device in thermal proximity to the ring. By thermal proximity is meant that the mixture is placed close enough to the ring, and preferably in contact therewith such that exposure of the ring to inductive currents causes induced heating in the ring which heat is transferred to the mixture causing first release of gas from the gas-releasing material and then evaporation of the evaporable getter metal and further gas release.

The gas-releasing material and the getter metal can be in any physical form but are generally particulate, and are preferably pressed together to form a cohesive mass. The gas-releasing material can be present in any amount which will release the gas in order to effect distribution of the getter metal film, and in the case of an active gas not saturate the getter metal. The gas-releasing material can be admixed with the getter metal in widely varying weight ratios, but generally is present in ratios of 0.5:100 to 50:100, and preferably 1:100 to 10:100, parts by weight of gas-releasing material per part by weight of getter metal. The gas-releasing material is generally present in an absolute amount sufficient to produce a pressure of 5×10^{-4} to 5×10^{-1}, and preferably 10^{-3} to 5×10^{-2} torr.

According to the present invention a second gas-releasing material is provided adapted to release its gas during the latter period of getter metal evaporation. This is preferably accomplished by placing this gas-releasing material at a point remote from the ring such that it is heated after the ring is heated thereby releasing the gas from this source during the latter period of getter metal evaporation. By so constructing the getter devices it is possible to employ existing cathode-ray tube manufacturing techniques even with these novel devices. The second gas-releasing material can be present in widely varying amounts as long as the total gas released from the first and second sources combined does not consume too great a capacity of the getter metal film. In general, the volume ratio of the gas produced by the second source to that produced by the first source is 1:10 to 10:1.

Referring now to the drawings, and in particular FIGS. **1** and **2**; there is shown a getter device **20** of the present invention. The device **20** comprises a ring **21**, a pressed particulate mixture **22** comprising barium-aluminum alloy and nickel and Fe_4N in contact with the ring **21**. Attached to the ring **21** is a disc-shaped shield **23** of a heat conductive material. The shield **23** substantially closes the area circumscribed by the ring **21**. The shield **23** has a coaxial depression **24** which functions as a holder containing an amount of a gas-releasing material **25**.

The ring **21** comprises an upper extending segment **26** and a horizontally extending segment **27**. Attached to the ring **21** by means of a plurality of tabs **28**, is a heat insulative base **29**. The getter device **20** is also provided with a second tab **30** to facilitate mounting of the device **20** in the tube as described more completely below. In order to minimize heat transfer between the shield **23** and the base **29**, the shield is provided with a plurality of depressions **31**.

Referring now to FIGS. **3** and **4**, there is shown a modified getter device **40** similar in many respects to the device 20 except that a holder 41, in the shape of conical cup is positioned coaxially on the shield 42, a gas-releasing material 43 is within the holder 41. The remaining structural elements are identical to those of the device 20.

Referring now to FIGS. 5 and 6, there is shown another modified device 50 of the present invention. The device 50 comprises an annular ring 51 of an inductively heatable material. In the ring 51 is a mixture 52 of a gas-releasing material and an evaporable getter metal. Attached to the ring 51 and extending upwardly therefrom, is a support member 53, the top portion of which is bent into a horizontal segment 54. Attached to the horizontal segment 54 is a cylindrical holder 55 containing a gas-releasing material 56.

Referring now to FIG. 7, there is shown another modified device 60 of the present invention. The device 60 comprises an annular ring 61 of an inductively heatable material, a mixture 62 of a gas-releasing material and an evaporable getter material in the ring 61. The device 60 further comprises a support member 63, having an upper horizontally extending segment 64 and a lower horizontally extending segment 65 connected by a vertical segment 66. The upper segment 64 is attached to the ring 61 by any convenient means such as by spot welding. Attached to the vertical segment 66 is a holder 67 similar to the holder 55 of FIG. 6. The holder 67 contains a gas-releasing material not shown.

Referring now to FIG. 8, there is shown a partial sectional view of a cathode-ray tube 70 having a screen not shown and an electron gun 71. Attached to the gun 71 is a flexible metallic strip 72 which is attached on its other end to the tab 30 of the getter device 20. The strip 72 is spring biased such that the base 29 of the device 20 rests on the wall 73 of the tube 70.

According to the process of the present invention, the getter device 20 is placed within the tube 70, whereupon the tube 70 is evacuated by any convenient means, and then sealed. A toroidal coil 74 is then positioned coaxially with the device 20 and current passed through the windings of the coil 74 from a source of high frequency alternating current not shown. The coil 74 generates lines of force shown schematically as lines 75 and 76 creating a toroidal field. Because the ring 21 of the device 20 lies almost completely within the toroidal field, the ring 21 is rapidly heated. This heat, together with the heat induced by the field in the material 22, causes the material 22 to increase its temperature until the Fe_4N thermally decomposes, releasing nitrogen in the tube 70 and raising the internal pressure in the tube to within 10^{-3} to 5×10^{-2} torr. Continued application of power to the coil 74 continues to increase the temperature of the material 22 until the getter metal begins to evaporate and begins to deposit on the inside surface of the tube 70. However, because the depression 24 (see FIG. 2) containing the gas-releasing material 25 is in the weaker portion of the toroidal field, this gas-releasing material releases its gas only at a later point in time and according to the present invention during the latter period of getter metal evaporation.

Referring to FIG. 9, there is shown the mounting method for getter devices 50 and 60. The cathode-ray tube 80 has an electron gun 81 to which is attached a support 82 holding the getter device 50 coaxially in the neck 83 of the tube 80. A toroidal coil 84 is positioned around the neck 83 of the tube 80, and is therefore coaxial with the getter device 50. Current is passed through the coil 84 from a source not shown, creating lines of force 85 and 86 which causes first thermal decomposition of the gas-releasing material admixed with the getter metal, and then onset of getter metal evaporation followed by release of gas from the gas-releasing material in the holder 55 which occurs at a later time because of its position on the periphery of the toroidal field.

As used herein, "cc-torr" and "ltr-torr" refer to the quantity of gas respectively in cubic centimeters or liters when measured at a pressure of 1 torr. One torr is a pressure equal to that exerted by a column of mercury 1 mm high. One micron (μ) is a pressure equal to that exerted by a column of mercury 0.001 mm high.

The invention is further illustrated by the following examples in which all parts and percentages are by weight unless otherwise indicated. These non-limiting examples are illustrative of certain embodiments designed to teach those skilled in the art how to practice the invention and to represent the best mode contemplated for carrying out the invention.

EXAMPLE 1

This comparative example illustrates the gas-releasing character of prior devices. A typical prior art getter device designated Device A, identical in all respects to the getter device 20 but having no gas-releasing material 25, is placed in a cathode-ray tube in the position shown in FIG. 8. In Device A, the mixture 22 consists of 460 mg of an alloy containing 56 percent barium, balance aluminum; 516 mg nickel; and 24 mg of Fe_4N. Complete decomposition of the Fe_4N would release 850 cc torr of N_2. Current is passed through the coil and the getter device 20 heated while measuring the gas pressure within the tube and the amount of getter metal, which in this case is barium, evaporated from Device A. These variables are plotted as a function of time in FIG. 10. As can be seen by reference to FIG. 10, less than one-half of the barium is evaporated in the presence of gas.

EXAMPLE 2

The procedure of Example 1 is repeated employing the same times, temperatures, conditions, and devices except that the device 20 designated Device B, having the gas-releasing material 25, is employed whereupon the graph shown as FIG. 11 results. As can be seen by this figure, the gas pressure exhibits a second peak due to release of gas from the gas-releasing material 25. Furthermore, this second period of gas release occurs during the latter half of the period of barium evaporation.

EXAMPLE 3

This example illustrates the increased sorptive speed and sorptive capacity of the getter devices of the present invention.

A getter device termed Device C, identical to Device A of Example 1 but having 48 mg of Fe_4N admixed with the nickel and barium-induction barium-aluminum alloy, is placed in a cathode-ray tube and subjected to induction heating as described with reference to FIG. 8, in order to evaporate the barium. Thereafter, carbon monoxide is introduced into the tube at a controlled rate equal to the rate at which it is sorbed by the barium film. The sorption speed in cc/sec is plotted as a function of the quantity of carbon monoxide sorbed in ltr - torr and the speed is measured at the pressure of 1×10^4 torr. The results are displayed graphically in FIG. **12** as line **91**. FIG. **12** is a semi-log plot. The procedure is repeated except that Device C is replaced by Device D, having the same total Fe_4N (48 mg), but wherein 24 mg are mixed with the nickel, barium-aluminum alloy mixture and 24 mg are placed in the depression **24** as shown in FIGS. **1** and **2**. The results are recorded in FIG. **12** as line **92**. As can be seen by reference to FIG. **12**, the getter devices of the present invention, characterized by the line **92**, have a greater capacity of carbon monoxide and maintain their sorptive speed for a greater length of time than do prior getter devices characterized by line **91**. For example, the sorptive capacity of barium film produced by the Device C (line **91**) begins to decrease after sorption of about 3 ltr-torr of CO, whereas that of the Device D (line **92**) maintains its initial speed until it has sorbed about 4 ltr-torr of CO. Furthermore, after sorbing 8 ltr-torr of CO, the film from the Device C (line **91**) is sorbing at a rate of only 10^5 cc/sec, whereas that of Device D (line **92**) is 7×10^5 cc/sec, or seven times as great. this is true although both devices initially contained exactly the same amount of getter metal (240 mg barium), and exactly the same amount of gas-releasing material (48 mg of Fe_4N).

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described above and as defined in the appended claims.

I claim:

1. A process for depositing a getter metal on the inside walls of a cathode-ray tube comprising the steps of:
- I. placing within the cathode-ray tube
  - a. a source of getter metal vapor
  - b. a first gas source and
  - c. a second gas source and then;
- II. evacuating the cathode-ray tube and then;
- III. sealing the tube and then;
- IV. releasing gas from the first gas source and then;
- V. evaporating the getter metal;
- VI. releasing gas from the second gas source during the period of getter metal evaporation.

2. The process of claim **1** wherein the gas pressure during step IV is between 10^{-3} and 5×10^{-2} torr.

3. The process of claim **1** wherein the gas is nitrogen.

4. The process of claim **1** wherein the gas is nitrogen in Step IV and is hydrogen in Step VI.

5. The process of claim **1** wherein the getter metal is barium.

6. The process of claim **1** wherein Steps IV, V, and VI are effected by heating the source of getter metal vapor and the two gas sources by means of an inductive field.

7. The process of claim **1** wherein the sources of gas are Fe_4N.

8. The process of claim **1** wherein Step II is practiced while heating the cathode ray tube to superambient temperatures up to 400° C.

9. A process for depositing barium metal on the inside walls of a cathode-ray tube comprising the steps of:
- I. placing within the cathode-ray tube
  - a. a source of barium vapor
  - b. a first source of nitrogen
  - c. a second source of nitrogen
- II. evacuating the cathode-ray tube and then;
- III. sealing the tube and then;
- IV. releasing nitrogen from the first source and then;
- V. evaporating the barium
- VI. releasing nitrogen from the second source during the period of barium evaporation.

10. A process for depositing a getter metal on the inside walls of a cathode-ray tube comprising the step of;
- I. providing a cathode-ray tube with a getter device having:
  - a. a getter metal which is evaporable when heated by an inductive field,
  - b. a first source of gas which gas is released when its source is heated by an inductive field,
  - c. a second source of gas which gas is released when its source is heated by an inductive field,
- II. positioning an inductive field in operative relationship to the getter device wherein the portion of the field causing most rapid heating is positioned adjacent the first source of gas and wherein that portion of the field causing less rapid heating is positioned adjacent the second source of gas whereby gas is released from the first source prior to getter metal evaporation and gas is released from the second source during getter metal evaporation.

* * * * *