

[54] GENERATION OF METAL VAPORS

[72] Inventors: Paolo Della Porta; Mario Zucchinielli; Elio Rabusin; Carlo Emili, all of Milan, Italy

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

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[58] Field of Search 417/48, 49, 51; 313/174, 180, 313/7; 315/108; 250/84.5; 316/25

[56] References Cited

UNITED STATES PATENTS

2,154,131 4/1939 Lederer 417/51 X

2,640,949 6/1953 Cook 313/180 X
3,102,633 9/1963 Baronetzky.....417/51
3,366,820 1/1968 Wolf 313/174 X

Primary Examiner—Robert M. Walker

Attorney—Burns, Doane, Benedict, Swecker & Mathis

[57] ABSTRACT

A particle free device for releasing a metal vapor, such as cesium or mercury, which comprises a vapor permeable particle free envelope and a metal vapor releasing substance within the envelope. This substance can be a mixture of a metal compound and reducing agent for the compound, or can be a material such as a metal oxide which releases its metal upon heating. The devices can have a resistance heating unit in thermal proximity to the metal vapor releasing substance. These devices are useful for the introduction of metal vapors into vessels such as electron tubes.

4 Claims, 7 Drawing Figures

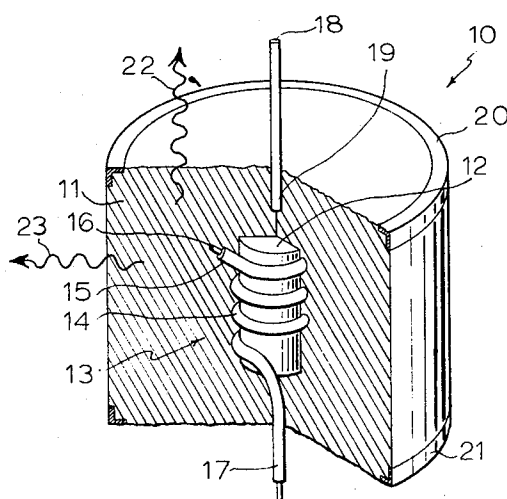


FIG. 1

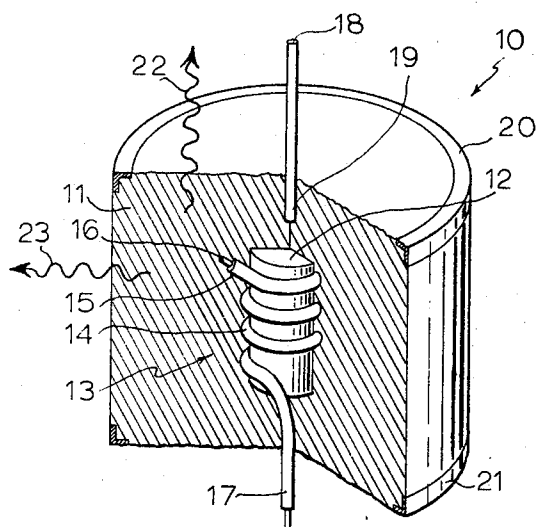


FIG. 2

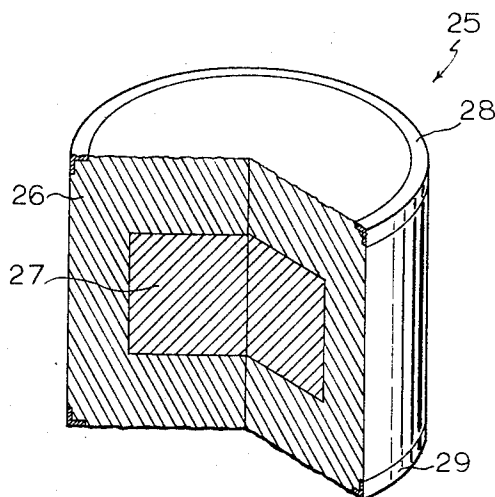


FIG. 3

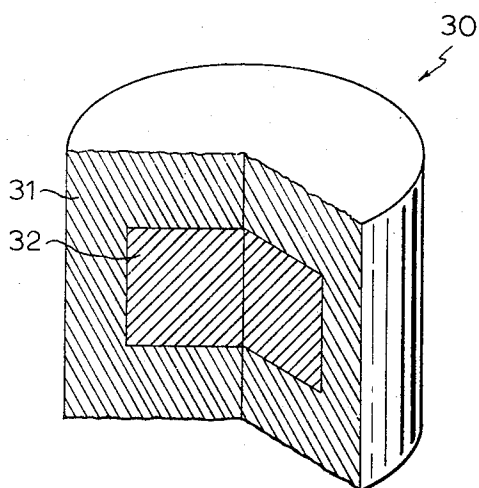
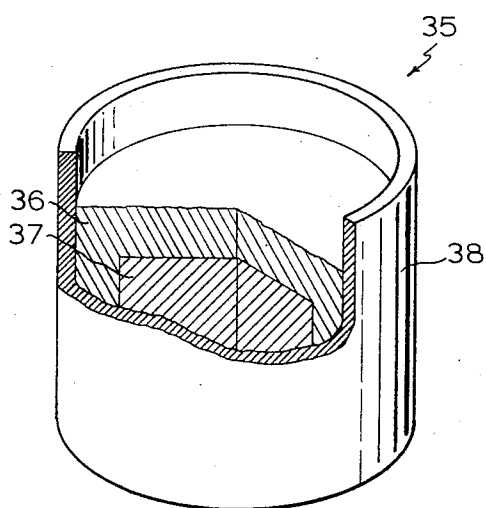


FIG. 4



INVENTORS

Paolo della Porta
Mario Zucchinelli
Elio Rabusin
Carlo Emili

FIG. 5

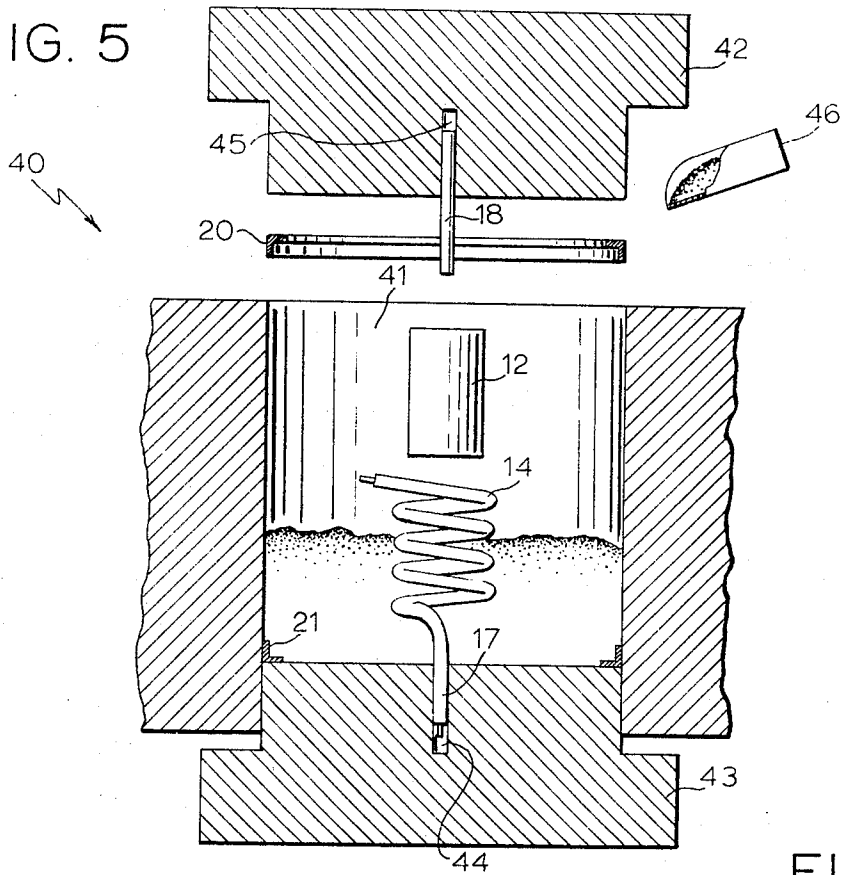


FIG. 6

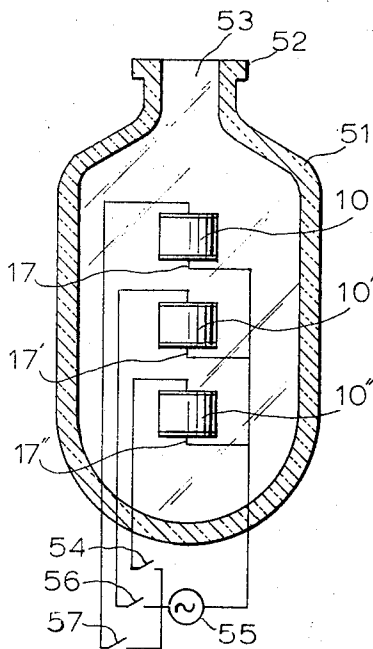
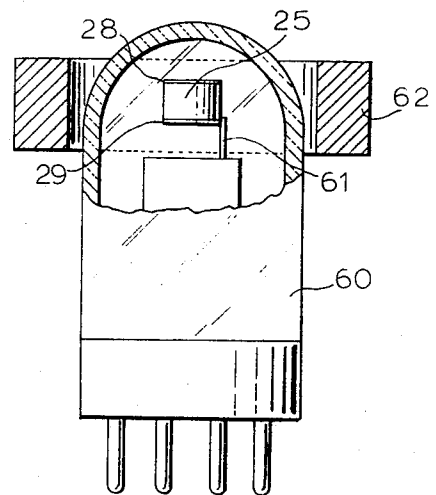


FIG. 7



INVENTORS

Paolo della Porta
Mario Zucchinelli
Elio Rabusin
Carlo Emili

GENERATION OF METAL VAPORS

Devices which release metal vapors, such as those of mercury, cesium, potassium, or sodium, in vessels such as electron tubes are well-known in the art as described, for example, in della Porta et al., U.S. Pat. No. 3,385,644; Italian Pat. No. 784,903; Italian Complete application 21508 A/67 of Nov. 12, 1967; and by Eichenbaum, et al., "Cesium Vapor Dispenser," *The Review of Scientific Instruments*, Vol. 35, No. 6, June 1964, pp. 691-693. Unfortunately, the above and other prior art devices suffer from a number of disadvantages. For example, they frequently release small particles before, during and/or after metal vapor release. These small particles are electrically conductive and can cause short circuits, damage photosensitive surfaces and cause other difficulties within the electron tubes. Many of these devices require a high amperage for activation of the metal vapor releasing substance. Still others release a large amount of noxious gases such as oxygen when activated.

Certain prior mercury releasing devices exhibit some special problems. In della Porta et al. supra there is disclosed a mercury releasing substance comprising a mixture of mercuric oxide and a zirconium-aluminum alloy. Such a mixture has been found to be eminently suitable for releasing from about 1 to about 10 mg of mercury. However, difficulties have been encountered in attempting to employ this mixture to produce more than about 10 mg of mercury. This is because the reduction of mercuric oxide with the zirconium-aluminum alloy is an exothermic reaction. When the mixture of mercuric oxide and alloy has a small mass it is possible to dissipate the exothermic heat of reaction from the mass. However, when the mass is increased without a consequent increase in the radiation surface area, the reaction becomes explosive due to the increased temperature of the mixture. Increasing the heat radiation surface has proved impractical. In some cases since the resultant devices are frequently larger than the tubes in which they are to be placed.

Accordingly, it is an object of the present invention to provide improved metal vapor releasing devices which are substantially free of one or more of the disadvantages of prior devices.

Another object is to provide improved metal vapor releasing devices which are substantially free from loose particles.

A further object is to provide devices which can be activated at low amperages.

A still further object is to provide devices which release metal vapors substantially free of oxygen and other noxious gases.

Yet another object is to provide devices which function as a non-evaporable getter before, during, and/or after metal vapor release.

Still another object is to provide particle free devices for releasing alkali metal vapors which devices function as a re-activatable non-evaporable getter device after metal vapor release.

Still another object is to provide a single improved generator for releasing a plurality of alkali metals such as cesium, potassium, and sodium.

Still another object is to provide improved devices which release mercury, and especially over 10 mg of mercury.

Still another object is to provide an improved method for manufacturing particle free metal vapor releasing 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 sectional view in perspective of one embodiment of a metal vapor releasing device of the present invention employing a resistance heating unit;

FIGS. 2, 3, and 4 are sectional views in perspective of other embodiments of metal vapor releasing devices of the present invention designed to be heated by induction currents;

FIG. 5 is a sectional view illustrating the preferred method of manufacturing the devices of the present invention;

FIG. 6 is a sectional schematic representation of an alkali metal generator of the present invention in which are shown

on a smaller scale than FIGS. 1 through 5; metal vapor releasing devices shown in these figures;

FIG. 7 is a sectional view of a vacuum tube employing a metal vapor releasing device of the present invention.

According to the present invention there is provided a particle free device for releasing a metal vapor which comprises a vapor permeable particle free envelope of a cohesive particulate material and a metal vapor releasing substance. In one preferred embodiment the metal vapor releasing substance comprises a compound of the metal and a reducing agent for the compound. In another preferred embodiment, the metal vapor releasing substance comprises a thermally degradable compound of the desired metal. In yet another preferred embodiment, the device further comprises a resistance heating unit in thermal proximity to the metal vapor releasing substance.

The devices of the present invention are particle free before, during, and after metal vapor release. The major source of particles in prior devices is the particulate metal vapor releasing substance which becomes fractured when the metal vapor is released, usually by heating. In the present invention, the envelope of cohesive particulate material prevents any particles of the metal vapor releasing substance from leaving the device and entering the vessel to be supplied with the metal vapor.

The metal vapor releasing substance is encased in the envelope, at least a portion of which is formed of the metal vapor permeable cohesive particulate material. The particulate material is rendered cohesive by any convenient means, but preferably autogenously without the use of a binder such as by sintering, or more preferably, pressing at ambient or super-ambient temperatures until the particles of the particulate material are bonded to one another forming an envelope which is permeable to the metal vapor, but which is impermeable to particles released by the metal vapor releasing substance. Examples of suitable particulate materials include among others, copper, iron, nickel and stainless steel. In an especially preferred embodiment of the present invention, the particulate material is a non-evaporable getter material, examples of which include among others, titanium, niobium, barium, tantalum, zirconium, mixtures thereof, alloys thereof, and alloys of these metals with other metals which do not materially reduce the gettering capacity of the getter material. Zirconium-aluminum alloys are the preferred getter materials such as those having 5 to 30, and especially 13 to 18 weight percent aluminum, balance zirconium. Prior to being rendered cohesive the particulate material passes through a U.S. standard screen of 30 mesh/inch, and preferably passes through a screen of 100 mesh/inch, and is retained on a screen of 140 mesh/inch.

Virtually any metal in the periodic table which will evaporate when heated to a temperature less than, and preferably at least 50° C. less than the melting point of the cohesive particulate material, can be released by the devices of the present invention. One preferred class of metals is the alkali metals such as lithium, rubidium, sodium, potassium, cesium, and most especially the last three, as well as beryllium, magnesium, calcium, barium, and mercury.

The metal vapor releasing substance can be in any form which will release the desired metal when supplied with energy generally by heating. Examples of suitable metal vapor releasing substances include amalgams and alloys such as a barium aluminum alloy in admixture with nickel. One preferred class of metal vapor releasing substances is mixtures of a metal compound and a reducing agent for the compound. The metal compound can be any which is reducible to its metal at convenient temperatures such as 100° to 1,100° C. Classes of suitable metal compounds include oxides, sulfides and salts of mineral acids such as chromates, phosphates, pyrophosphates, sulfates, chlorides, and nitrates. Examples of suitable metal compounds include among others mercuric oxide, mercuric sulfate, mercuric sulfide, cesium dichromate, potassium chromate, rubidium chromate, cesium chloride,

barium carbonate, and magnesium sulfate. Any reducing agent can be employed which is compatible with the metal compound and will reduce it to its metal. Such reducing agents and their use with metal compounds is well-known in the art. Examples of suitable reducing agents include among others, calcium, magnesium, silicon, aluminum, and zirconium. In an especially preferred embodiment the reducing agent is chosen which is also one of the above-described non-evaporable getter materials, and especially the above-described zirconium-aluminum alloys. The reducible compound and reducing agent can be mixed in widely varying weight ratios, but a stoichiometric excess of reducing agent is usually employed.

The metal vapor releasing material can also be a compound which will thermally decompose to release its metal at elevated temperatures, and generally from 200° to 1,200° C, usually 300° to 1,000° C, and preferably from 400° to 900° C. The preferred alkali metal-releasing compounds are the alkali metal oxides such as KO_2 , Cs_2O , and Na_2O_2 . However, these alkali metal oxides are hygroscopic and are converted to hydroxides upon exposure to moist air. Additionally, carbon dioxide from the air changes these oxides to carbonates all of which are undesirable in the present invention because of concurrent release of water vapor, and/or carbon dioxide with the metal vapor. Therefore, the use of these oxides requires the use of controlled atmospheres which are free of carbon dioxide and water vapor in order to produce the devices of the present invention. The preferred mercury releasing substance is mercuric oxide (HgO) which does not react with carbon dioxide or water vapor and thus can be employed without the use of special atmospheres. The metal vapor releasing substance including the metal compound and the reducing agent are finely divided, and generally pass through a U.S. Standard screen of 30 mesh/inch, and preferably pass through a screen of 100+ mesh/inch, and are retained on a screen of 600+ mesh/inch.

Referring now to the drawings, and in particular to FIG. 1, there is shown a non-limiting preferred embodiment of the present invention in the form of a metal vapor releasing device 10, comprising a vapor permeable particle free envelope 11. Within the envelope 11 is a mixture of an alkali metal compound and a reducing agent for the compound which mixture has been pressed into the form of a pellet 12. The pellet 12 is surrounded by a heating unit 13 comprising a helically coiled wire 14 surrounded by a high temperature resistant coating 15. The inner end 16 of the wire 14 is free of coating 15, and is in electrical contact with the particulate material of the envelope 11. Also extending outside the envelope 11 is a conductor 18, the end 19 of which is in electrical contact with the material of the envelope 11. The device 10 is provided with an upper circular L-shaped retaining ring 20, and a lower circular L-shaped retaining ring 21. The rings 20 and 21 provide the device 10 with a hard chip-resistant edge further reducing the tendency of the device 10 to release particles.

In operation the device 10 is placed in a tube or vessel to be charged with a metal vapor. The tube is then closed and evacuated by any convenient means such as a diffusion pump, or a sputter-ion pump. Potential is then impressed across the conductor 18 and the end 17 of the wire 14. The potential causes current to flow through the wire 14 to its end 16 through the material of the envelope 11 to the end 19 of the conductor 18 and then out of the device 10. This flow of current causes heating of the wire 14, which heats the pellet 12, causing the reducing agent to reduce the alkali metal compound and release an alkali metal vapor which then escapes from the device 10 through the envelope 11 in all directions as shown by arrows 22 and 23.

The end 19 of the conductor 18 can be directly connected to the end 16 of the wire 14, but is preferably separated as shown in FIG. 1 to facilitate construction of the device as described below and eliminate the need for exact alignment of the parts. The wire 14 can be bare, but is preferably provided with a dielectric coating 15 in order to insulate the wire 14 if

the envelope 11 is electrically conductive. The wire 14 can be any material of high ohmic resistance such as tungsten, tantalum, or the widely used high resistance material sold under the tradename Nichrome. The conductor 18 can be of like materials, but is preferably a readily weldable material of low electrical resistance such as molybdenum.

Referring now to FIG. 2 there is shown a device 25 similar in many respects to the device 10, but having no heating element therein. The device 25 comprises an envelope 26 surrounding a metal vapor releasing material 27. The device 25 is provided with rings 28 and 29.

FIG. 3 shows a similar device 30 with envelope 31, and metal vapor releasing material 32, but having no rings.

FIG. 4 shows a device 35 comprising an envelope 36, and a metal vapor releasing material 37, both contained within a cylindrical container 38.

Referring now to FIG. 5, there is schematically shown the preferred method for manufacturing the devices of the present invention. The device 10 is preferably formed in an apparatus 40 comprising a cylinder 41, having slidably mounted therein an upper piston 42 and a lower piston 43. To form the devices 10, approximately one-half of the particulate material which will eventually form the envelope 11 is placed in the cylinder 41 along with the ring 21 if such is to be provided. The helical coil of wire 14 is positioned in the cylinder 24 with the end 17 projecting into a hole 44 in the lower piston 43. The conductor 18 is fitted into a hole 45 in the upper piston 42. The cylinder 12 is then placed within the helix of the wire 14, and the other half of the particulate material added as shown schematically by the partially cut-away scoop 46. The upper ring 20 is then placed in the cylinder 24 and the upper piston 42 downwardly moved to compress the particulate material and form the device 10 having the vapor permeable particle free envelope 11 as shown in FIG. 1.

The device 25 is similarly formed except that the wire 14 and conductor 18 are omitted. The device 30 omits these as well as the rings 20 and 21. To form the device 35 the container 38 is first placed in the cylinder 41.

Referring now to FIG. 6, there is shown a generator 50 employing the metal vapor releasing devices 10 of the present invention. The generator 50 comprises an enclosure 51 having a rim 52 defining an opening 53 adapted to attach the generator 50 to the vessel to be supplied with the alkali metal vapors. Residing within the enclosure 51 are three devices, 10, 10' and 10'', identical except that the alkali metal compound in pellet 12 of the device 10 is cesium, whereas it is sodium in the device 10' and is potassium in the device 10''. The device 10 is connected in series circuit with a switch 54 and a power source 55 by means of the wire 17 and the conductor 18. The devices 10' and 10'' are likewise respectively connected in series with the power source 55 and switches 56 and 57.

In operation the generator is connected to the vessel to be evacuated by means of the rim 52 such that the opening 53 is in fluid communication with the vessel. Thereafter, the vessel and enclosure 51 are collectively evacuated by any convenient means such as sputter-ion pump or diffusion pump whereupon the switches 54, 56, and 57 are separately closed in order to release the cesium, potassium and sodium in the desired sequence in order to produce photosensitive surfaces within the vessel in a well-known manner.

Referring now to FIG. 7, there is shown the method of use of the devices 25, 30, and 35 of the present invention. The device 25, for example, is mounted in a tube 60 on any suitable support 61. The tube 60 is then evacuated through any suitable conduit not shown while maintaining the temperature of the tube and its contents at 300° to 500° C., and preferably 350° to 400° C. for a period of time in order to remove occluded gases. The tube 60 is then closed, permitted to cool, and surrounded by a toroidal coil 62. Current is passed through the coil 62, causing induction heating in the device 25, and especially the rings 28 and 29 thereof. This heat is transmitted to the metal vapor releasing material 27, (See FIG. 2) causing it to release its metal vapor and in certain

cases other gaseous decomposition reaction products such as oxygen. The metal vapor passes through the metal vapor permeable envelope 26 which traps the gaseous reaction products due to the non-evaporable getter character of the material of the envelope 26.

In general, the rings 20, 21, 28, 29 and the container 38 can be of any metal if their only function is to provide a chip-resistant edge to eliminate loose particles, however, the rings 28, 29 in the device 25, and the container 38 in the device 35 must be of an inductively heatable material such as iron, nickel, or stainless steel to facilitate induction heating of the devices 25 and 35.

Special advantages of the devices of the present invention are that the envelope 11, 26, 31, and 36 effectively form a thermal insulator which permits these devices to be placed in a vacuum tube and the entire assembly heated to a temperature above that at which the metal vapor releasing substance 27, 32, and 37 would normally release their metal vapor provided that the heating time is limited to a relatively short period of approximately 2 to 5 minutes. Therefore, it is possible to heat mercuric oxide containing devices to 525° C. or higher temperature for some minutes even though the decomposition temperature of mercuric oxide is 500° C. This thermal insulating feature of the devices of the present invention does not inhibit the use of high frequency alternating current in order to inductively heat the devices for the purposes of thermally decomposing the metal vapor releasing material. Furthermore, it has been found that when a reducing agent is present in admixture with mercuric oxide, some reduction, and therefore, some undesirable loss of mercury takes place even upon heating to 350° C. Therefore, in a preferred embodiment of the present invention, the gas releasing material contains no reducing agent, i.e., consists essentially of the thermally decomposable metal compound such as mercuric oxide, and the envelope is of a non-evaporable getter material which sorbs oxygen and/or other gaseous decomposition products of the metal compound.

Those embodiments wherein the envelope is constructed of a non-evaporable getter material exhibit two additional advantages. First, oxygen, water vapor, and other noxious gases are prevented from reaching the metal vapor releasing material. Second, the heating of the device in the tube, after liberating of the desired metal vapor, reactivates the getter material such that the device sorbs noxious gases after metal vapor release and throughout the life of the tube.

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 and are designed to teach those skilled in the art how to practice the invention and to represent the best mode presently known for carrying out the invention.

EXAMPLE I

One part of finely divided Cs_2CrO_4 which passes through a screen of 270 mesh/inch and is retained on a screen of 400 mesh/inch is intimately mixed with 2 parts of an alloy of 16 percent aluminum and 84 percent zirconium which passes through a screen of 100 mesh/inch and is retained on a screen of 400 mesh/inch. A portion of this mixture is then formed into a cylinder similar to the pellet 12 of FIG. 1 having a diameter of 2 mm and a length of 2 mm. The zirconium-aluminum alloy employed in this example is that available from S.A.E.S., Getters S.p.A., Milan, Italy, under the name St101.

A tungsten wire having a diameter of 0.2 mm is formed into a helix 15 mm long and having an inside diameter slightly larger than the diameter of the pellet 12. The helix is then sprayed with an aqueous solution of aluminum oxide which is then dried and baked at 1,200° C. The pellet 12 is then inserted into the helix.

Finely divided alloy of 16 percent aluminum and 84 percent zirconium which passes through a screen of 100 mesh/inch

and is retained on a screen of 140 mesh/inch is employed as described above with reference to FIG. 5 to form the envelope 11 of the device 10. The device is placed in a tube which is evacuated to a pressure of 10^{-6} torr, whereupon a current of 2.5 amps is passed through the wire for 10 minutes, releasing cesium.

EXAMPLE II

The procedure of Example I is repeated except that the cesium chromate is replaced by an equal weight of potassium chromate to produce a potassium releasing device.

EXAMPLE III

The procedure of Example I is repeated with the single exception that the cesium chromate is replaced by an equal weight of sodium chromate to produce a sodium releasing agent.

EXAMPLE IV

The procedure of Example I is repeated except that the zirconium-aluminum alloy used to construct the cylinder 12 is replaced by an equivalent weight of silicon of the same particle size.

EXAMPLE V

The procedure of Example I is repeated except that the alloy of zirconium and aluminum employed to form the envelope 11 is replaced by an equivalent weight of finely divided iron to produce a device having reduced gettering capacity, but being effective to limit loose particles which might otherwise be released by the cesium chromate and/or the reducing agent.

EXAMPLE VI

Finely divided mercuric oxide which passes through a screen of 270 mesh/inch and is retained on a screen of 400 mesh/inch is formed into a cylinder of the shape shown for the metal vapor releasing material 37 in FIG. 4. The pellet is then surrounded by an envelope of a finely divided alloy of 16 percent aluminum and 84 percent zirconium which passes through a screen of 100 mesh/inch and is retained on a screen of 600+mesh/inch. The resultant device has the structure of the device 35 of FIG. 4.

The device is placed in a tube and subjected to induction currents as shown in FIG. 7, whereupon pure mercury vapor free of oxygen is produced.

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.

What is claimed is:

1. A particle free device for releasing a metal vapor, said device comprising;

A. a vapor permeable, particle-free envelope of an autogenously bonded particulate metal;

B. a mixture of a reducible metal compound and a reducing agent for the compound, the mixture residing within the envelope; and,

C. a resistance heating unit in thermal proximity to the mixture;

whereby passing a current through the heating unit heats the mixture causing reduction of the metal compound by the reducing agent producing a metal vapor which escapes through the vapor-permeable envelope without releasing particles.

2. A particle free device for releasing an alkali metal in a vessel comprising:

A. an intimate mixture of a reducible compound of an alkali metal and a reducing agent for said compound;

B. a wire of high electrical resistance in thermal proximity with said mixture;

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- C. means for connecting the ends of said wire to a source of electrical current; and,
 - D. a vapor-permeable non-evaporable getter material completely surrounding said mixture.
3. A particle free device for releasing mercury vapor, said device comprising:
- A. a vapor permeable particle free envelope of a non-evaporable getter material;
 - B. mercuric oxide within the envelope.

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4. A particle free device for releasing over 10 mg of mercury, said device comprising:
- A. a vapor permeable particle free envelope of a particulate alloy of 84 percent zirconium, 16 percent aluminum;
 - B. a mercury releasing substance within the envelope, said substance consisting essentially of mercuric oxide containing over 10 mg of mercury.

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