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[73] Assignee **S.A.E.S. Getters S.p.A.**
Milan, Italy
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[33] **Italy**
[31] **31040/66 and 21538A/67**
Pat. 784903
Continuation-in-part of application Ser. No.
690,125, Dec. 13, 1967.

[54] **GENERATION OF ALKALI METALS**
20 Claims, No Drawings
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252/181.4, 252/181.6

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H01j 7/12
[50] **Field of Search..... 252/181.4,**
181.1, 181.3, 181.6, 181.7; 316/16

[56] **References Cited**
UNITED STATES PATENTS
2,117,735 5/1938 Lester 252/181.4X
3,385,644 5/1968 Della Porta et al. 316/16
Primary Examiner—Tobias E. Levow
Assistant Examiner—J. Cooper
Attorney—David R. Murphy

ABSTRACT: Compositions of matter which release alkali metal vapors comprising an alkali metal compound and a reducing agent for the compound wherein the reducing agent is an alloy of 5 to 30 weight percent aluminum balance zirconium. These compositions are useful in processes for the release of alkali metal vapors used in the production of photosensitive surfaces in vacuum tubes.

GENERATION OF ALKALI METALS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of parent application Ser. No. 690,125 filed Dec. 13, 1967 entitled "Metal Vapor Generators."

It is frequently desirable to provide electron tubes containing alkali metals such as cesium, potassium and/or sodium. For example, the alkali metals are employed to produce photosensitive surfaces such as those in television pickup tubes, photo multiplier tubes, electronic sights, image conversion tubes, and image intensifier tubes for radiological uses. The alkali metal is commonly introduced into such tubes by means of an alkali metal vapor dispenser containing a compound of the desired alkali metal and a reducing agent for the compound. Such a dispenser employing silicon as a reducing agent for cesium chromate is described in Eichenbaum et al. "Cesium Vapor Dispenser," *The Review of Scientific Instruments*, Vol. 35, No. 6, June 1964, pp. 691-693. Such dispensers are also described by Lester U.S. Pat. No. 2,117,735 (1938) who employs a mixture of cesium chromates as the alkali metal compound and as the reducing agent a mixture of zirconium powder and aluminum powder in a weight ratio of 8:1. Unfortunately, the alkali metal vapor releasing compositions of Eichenbaum and Lester and other prior compositions release an alkali metal vapor contaminated with noxious gases such as oxygen. These gases react with the alkali metal and reduce the photosensitivity of the resulting surface.

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

Another object is to provide compositions which release a substantially pure alkali metal vapor free of noxious gases such as oxygen.

A further object is to provide novel alkali metal releasing compounds employing a zirconium-aluminum alloy as the reducing agent wherein the alloy has advantages not realized by mixtures of the same metals.

Additional objects and advantages of the present invention will be apparent by the following detailed description thereof.

In the parent application composite structures are described which comprise a sintered matrix of a sinterizable material such as iron and within the matrix and alkali metal chromate and a zirconium-aluminum alloy as a reducing agent for the chromate. While such composite structures are effective for the purpose described, i.e., reduction of undesirable loose particles it has been discovered that the heating necessary to sinter the sinterizable material alters the composite structure in some unknown manner such that when the alkali metal vapor is later released it is contaminated with large quantities of noxious gases. In accordance with the present invention it has been discovered that compositions having no sinterized material and therefore those which consist essentially of an alkali metal compound and a zirconium-aluminum alloy release an alkali metal vapor which is substantially free of noxious gases. Zirconium-aluminum alloys of differing particle sizes have been employed as described in U.S. Pat. No. 3,385,644 admixed with mercuric oxide but have not heretofore been employed with alkali metal compounds as in the present invention. An additional advantage of the compositions of the present invention is that the zirconium-aluminum alloy need not be used in differing particle sizes.

The alkali metal compound can be any compound which is reducible to its metal by a reducing agent and is sufficiently stable alone and in admixture with its reducing agent to withstand the heat treatments commonly employed in the outgassing of vacuum tubes. Thus the preferred alkali metal compounds are those which are stable at temperatures up to 400° C. Examples of suitable alkali metal compounds include among others cesium chloride, sodium dichromate and most preferably cesium chromate, potassium chromate, sodium chromate, rubidium chromate and lithium chromate. The

chromates are greatly preferred over the dichromates because of the reduced amount of oxygen which they release.

The reducing agents employed in the present invention are zirconium-aluminum alloys and generally those of 5 to 30 weight percent aluminum balance zirconium, preferably those of 13 to 18 weight percent aluminum, balance zirconium and especially those of 16 percent aluminum and 84 percent zirconium produced as described in U.S. Pat. No. 3,203,901. It will be understood that minor amounts of other common impurities and compatible metals can be included in the alloy provided they do not materially affect the novel characteristics of the composition.

The alkali metal compound and the zirconium-aluminum alloy are both preferably employed as finely divided particles and generally those which pass through a screen of 100 mesh per inch and preferably those which pass through a screen of 270 mesh per inch. The iron or other sinterizable material when present also has these particle sizes.

The alkali metal compound and zirconium-aluminum alloy can be mixed in widely varying ratios but a stoichiometric excess of the zirconium-aluminum alloy is generally employed in order to completely reduce the reducible alkali metal compound and generally in ratios of 1:1 to 20:1 and preferably 3:1 to 10:1 parts by weight of alloy per part by weight of reducible compound.

According to another inseparable aspect of the present invention there is provided a process for releasing an alkali metal vapor in a vacuum. The composition of alkali metal compound and zirconium-aluminum alloy is placed in any metallic container capable of withstanding elevated temperatures. This container is then placed in a vacuum tube which is then evacuated mechanically or by any other suitable means while being maintained at 350° to 400° C. for 1 to 8 hours while evacuating residual gases. The container is then heated to the temperature of the onset of the reaction between the alloy and the alkali metal compound and generally between 450 and 1000° C. and preferably between 550 and 900° C. for a time sufficient to completely or partially reduce the alkali metal compound releasing the desired amount of alkali metal vapor.

The invention is further illustrated by the following examples in which all parts and percentages are by weight unless otherwise indicated. These nonlimiting 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 1

This example illustrates the small amount of gas released when cesium chromate is reduced with an alloy of 16 percent aluminum and 84 percent zirconium.

Into a mortar is placed 500 grams of a zirconium-aluminum alloy commercially available as St101 from S.A.E.S. Getters S.p.A. containing 16 percent aluminum and 84 percent zirconium. This alloy is ground with a pestle until it is a fine powder which passes through a screen of 270 mesh/inch, whereupon it is mixed with 100 grams of cesium chromate which has been similarly ground. A portion of this mixture is placed in a container of Nichrome V having a slit therein. The container is then placed in a vacuum tube and the entire assembly heated in a vacuum of 10^{-6} torr for 8 hours at 375° C. to remove residual gases. The assembly is cooled and then the container alone is heated to 600° C. whereupon cesium begins to evaporate. The temperature is increased in steps of 8° C/minute up to a maximum temperature of 850° C. This temperature is maintained for 1 minute. The cesium vapor deposits on the cold walls of the tube. During the period of cesium vapor release the tube is connected to a vacuum pump via a conduit containing a conductance which acts as a gas flow restricting orifice. The pressure on each side of the orifice is continuously recorded during the period of cesium

vapor release and the total quantity of gases released calculated according to the following formula:

$$Q = c \int_{t_0}^{t_1} [P_D(t) - P_P(t)] dt$$

wherein:

Q = the quantity of gas in cc.-torr

c = conductance of the orifice (146 cc./sec.)

P_D = pressure upstream of the conductance in torr

P_P = pressure downstream of the conductance in torr

t_0 = time at onset of cesium vapor release

t_1 = time at completion of cesium vapor release in seconds

dt = incremental time in seconds

The quantity of gas is found to be 0.3 cc.-torr/mg. of cesium chromate.

EXAMPLE 2

This comparative example illustrates the large amount of gas released by cesium chromate reduced with a mixture of one part by weight of aluminum and eight parts by weight of zirconium following the teaching of Lester supra.

The above procedure of example 1 is repeated employing the same times, temperatures, conditions and ingredients except that the zirconium-aluminum alloy is replaced by an equal weight of a mixture of one part by weight aluminum and eight parts by weight zirconium. The quantity of gas released is to be found to be 12 cc.-torr/mg. or approximately 40 times the amount of gas released in example 1 wherein the preferred zirconium-aluminum alloy is employed as the reducing agent.

EXAMPLE 3

The procedure of example 1 is repeated twice employing the same times, temperatures, components and conditions the first time with the exception that the cesium chromate is replaced by a stoichiometrically equivalent amount of sodium chromate and the second time with the exception that the cesium chromate is replaced by a stoichiometrically equivalent amount of potassium chromate. Similar results are obtained with low quantities of gas being evolved with the sodium or potassium vapor.

As used herein the term "cc.-torr" refers to the volume of gas in cubic centimeters at a pressure of one torr (1 mm. Hg. absolute) and is independent of the pressure. As can be seen by comparing example 1 and 2 the compositions of Lester release 40 times the amount of undesirable gas released by the compositions of the present invention.

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.

We claim:

1. A composition of matter useful for generating an alkali metal in a vacuum, said composition of matter consisting of an alkali metal compound which is reducible to its metal and which is stable up to 400° C and a zirconium-aluminum alloy as a reducing agent for the alkali metal compound wherein the zirconium-aluminum alloy contains 5 to 30 weight percent aluminum balance zirconium wherein the alloy and the alkali metal compound are present in a weight ratio of 1:1 to 20:1.

2. A composition of claim 1 wherein the compound of the alkali metal is an alkali metal chromate.

3. A composition of claim 1 wherein the compound of the alkali metal is selected from the group consisting of cesium chromate, potassium chromate and sodium chromate.

4. A composition of claim 1 wherein the zirconium-aluminum alloy is present in excess of stoichiometry.

5. A composition of claim 1 wherein the zirconium-aluminum alloy contains 16 percent aluminum and 84 percent zirconium.

6. A composition of matter for releasing an alkali metal vapor, in a vacuum said composition consisting of:

a. an alkali metal chromate and

b. an alloy of 5 to 30 weight percent aluminum balance zirconium present in excess of stoichiometry.

7. A composition of matter for releasing an alkali metal vapor, in a vacuum said composition consisting essentially of:

a. an alkali metal chromate and

b. an alloy of 13 to 18 weight percent aluminum, balance zirconium present in excess of stoichiometry.

8. A composition of matter useful for generating an alkali metal vapor in a vacuum, said composition consisting essentially of an alkali metal chromate and an alloy of 16 percent aluminum and 84 percent zirconium wherein the weight ratio of alloy to chromate is from 3:1 to 10:1 and wherein the alloy and the chromate are both finely divided such that they pass through a U.S. standard screen of at least 100 mesh per inch.

9. A composition of matter useful for generating an alkali metal vapor in a vacuum, said composition consisting essentially of cesium chromate and an alloy of 16 percent aluminum and 84 percent zirconium wherein the weight ratio of alloy to chromate is from 3:1 to 10:1 and wherein the chromate are both finely divided such that they pass through a U.S. standard screen of at least 100 mesh per inch.

10. A composition of matter useful for generating an alkali metal in a vacuum, said composition of matter comprising an alkali metal compound which is reducible to its metal and which is stable up to 400° C and a zirconium-aluminum alloy as a reducing agent for the alkali metal compound wherein the zirconium-aluminum alloy contains 5 to 30 weight percent aluminum balance zirconium wherein the alloy and the alkali metal compound are present in a weight ratio of 1:1 to 20:1.

11. A composition of claim 10 wherein the compound of the alkali metal is an alkali metal chromate.

12. A composition of claim 10 wherein the zirconium-aluminum alloy is present in excess of stoichiometry.

13. A composition of claim 10 wherein the zirconium-aluminum alloy contains 16 percent aluminum and 84 percent zirconium.

14. A composition of matter for releasing an alkali metal vapor, in a vacuum said composition comprising:

a. an alkali metal chromate and

b. an alloy of 5 to 30 weight percent aluminum balance zirconium present in excess of stoichiometry.

15. A process for releasing an alkali metal in a vacuum tube comprising heating to a temperature sufficient to release an alkali metal, a finely divided mixture consisting essentially of an alkali metal chromate which is stable up to 400° C. and a zirconium-aluminum alloy wherein the zirconium-aluminum alloy contains 5 to 30 weight percent aluminum balance zirconium wherein the alloy and the alkali metal chromate are present in a weight ratio of 1:1 to 20:1.

16. The process of claim 15 wherein the zirconium-aluminum alloy is present in excess of stoichiometry.

17. The process of claim 15 wherein the zirconium-aluminum alloy contains 13 to 18 weight percent aluminum balance zirconium.

18. The process of claim 17 wherein the zirconium-aluminum alloy contains 16 percent aluminum and 84 percent zirconium.

19. A process of claim 15 for releasing an alkali metal vapor in a vacuum tube comprising in sequence the steps of:

I. introducing into the tube a composition of matter of an alkali metal chromate and an alloy of 13 to 18 weight percent zirconium, balance aluminum present in excess of stoichiometry;

II. closing the tube and connecting it to a vacuum pump;

III. heating the tube at 300° to 400° C for 1 to 8 hours while evacuating residual gases; and

IV. heating the composition of matter at 550° to 900° C. to release the alkali metal vapor.

20. A process for releasing an alkali metal vapor in a vacuum tube comprising in sequence the steps of:

I. introducing into the tube a composition of matter of an alkali metal chromate and an alloy of 5 to 30 weight percent zirconium, balance aluminum wherein the alloy and

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the alkali metal chromate are present in a weight ratio of
1:1 to 20:1;
II. closing and evacuating the tube;

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III. heating the tube to evacuate residual gases; and
IV. heating the composition of matter to release the alkali
metal vapor.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,578,834 Dated May 18, 1971

Inventor(s) Paolo della Porta, Elio Rabusin

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 63, "Ad" should be "An"

Column 2, line 65, " 10^{16} " should be " 10^{-6} "

Signed and sealed this 28th day of September 1971.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents