United States Patent

Takashio et al.

[15] **3,644,101**

[45] **Feb. 22, 1972**

[54] CESIUM EVAPORATOR

[72] Inventors: **Haruo Takashio**, Tokyo; **Takayoshi Matsuzawa**, Yokohama-shi, both of Japan

[73] Assignee: **Tokyo Shibaura Electric Co., Ltd.**, Kawasaki-shi, Japan

[22] Filed: **June 6, 1968**

[21] Appl. No.: **734,963**

[30] **Foreign Application Priority Data**

June 10, 1967 Japan.....42/36770

[52] **U.S. Cl.**.....**23/294,** 117/225, 75/66

[51] **Int. Cl.**.....**B44d 1/02,** C23d 1/02

[58] **Field of Search**.....117/107, 106, 34, 107.2, 223, 117/224, 225; 75/66, 63; 23/294; 350/257; 252/188.3

[56] **References Cited**

UNITED STATES PATENTS

1,224,339	5/1917	Darrah	117/107
1,835,118	12/1931	Marden et al	75/66
1,966,220	7/1934	Rentschler	75/66
1,966,254	7/1934	Marden et al	75/66
3,468,807	9/1969	Spangenberg	75/66
3,468,806	9/1969	Niewold	75/66

Primary Examiner—Norman Yudkoff
Assistant Examiner—S. Silverberg
Attorney—George B. Oujevolk

[57] **ABSTRACT**

Cesium evaporator filled with a mixed powder of a silicon and cesium chromate and/or cesium bichromate for depositing cesium vapor on the face plate of a photoelectric tube, the silicon powder has such a particle size distribution that the average particle size is 30 to 80 microns, with particles larger than 100 microns or those smaller than one micron constituting not more than 30 weight percent, and the cesium chromate or cesium bichromate powder has such a particle size distribution that the average particle size is 3 to 10 microns with particles larger than 25 microns constituting not more than 30 weight percent and those smaller than 0.5 micron constituting not more than 40 weight percent.

1 Claims, 8 Drawing Figures

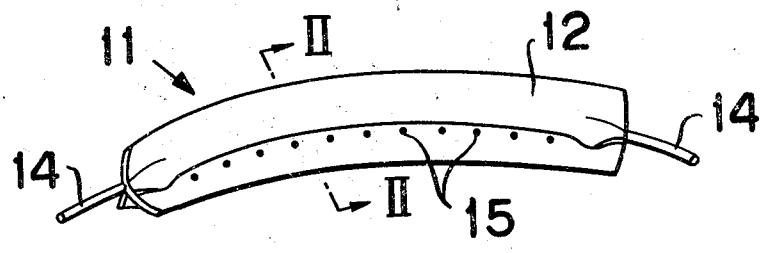


FIG. 1

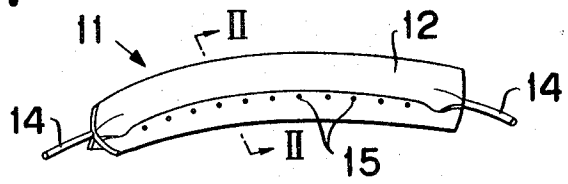


FIG. 3

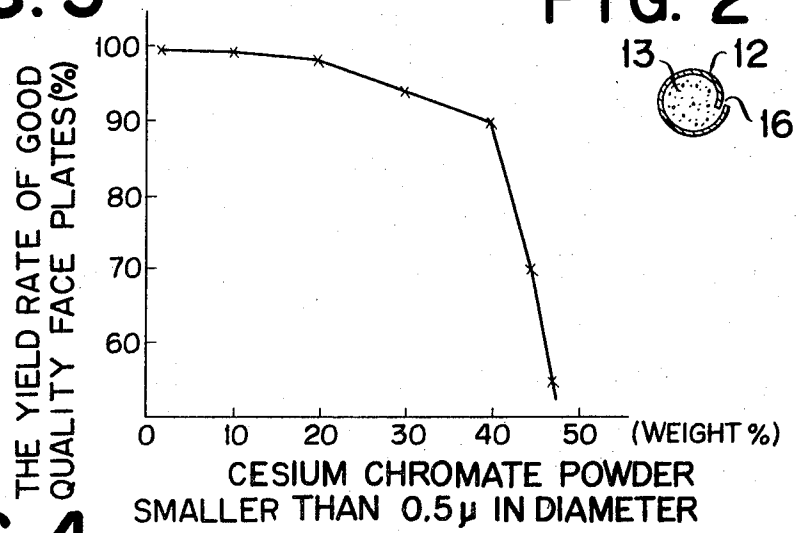
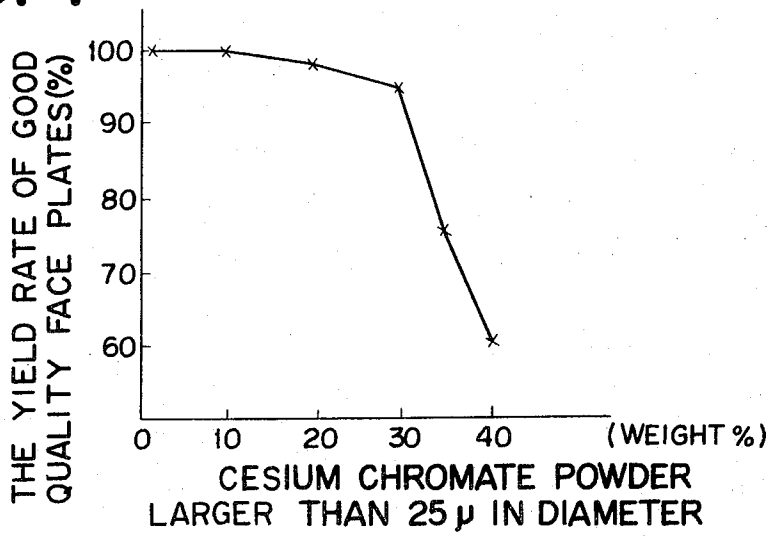


FIG. 2

FIG. 4



Harumo Takeshita
Takayoshi Matsuzawa
INVENTORS

BY George B. Cuyjoak
Attorney

FIG. 5

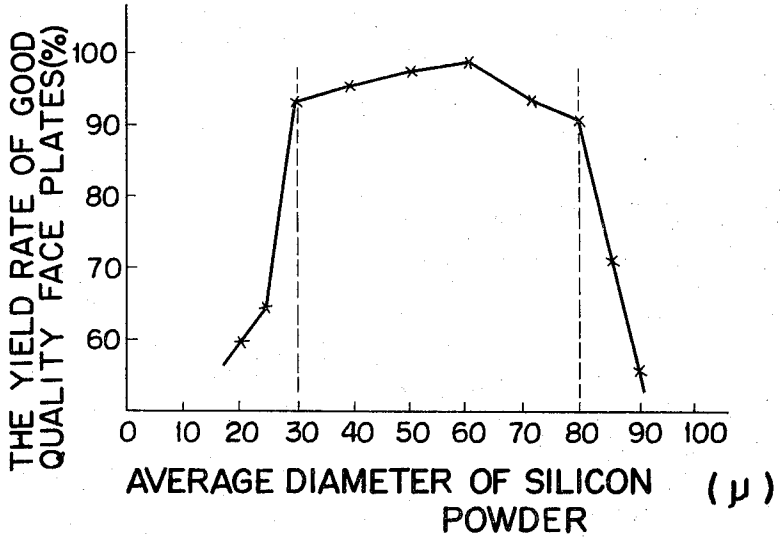


FIG. 6

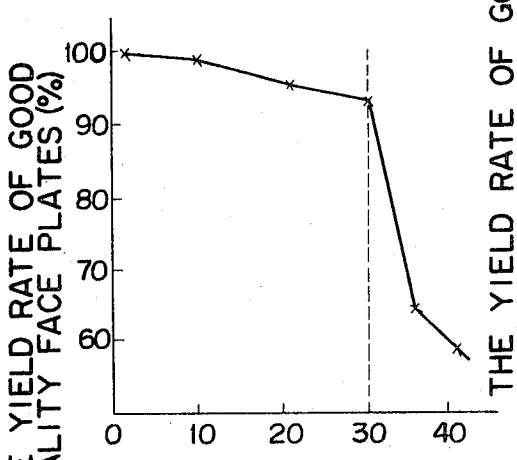
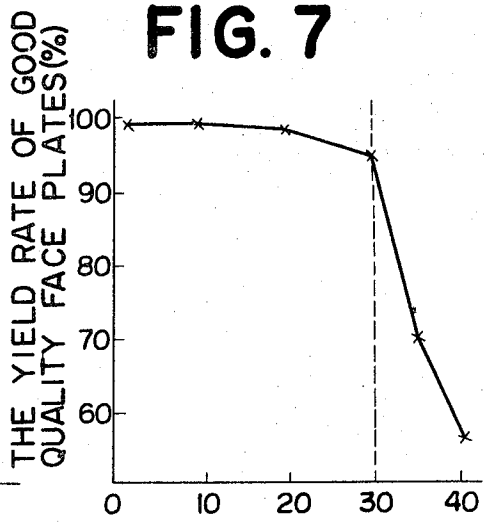
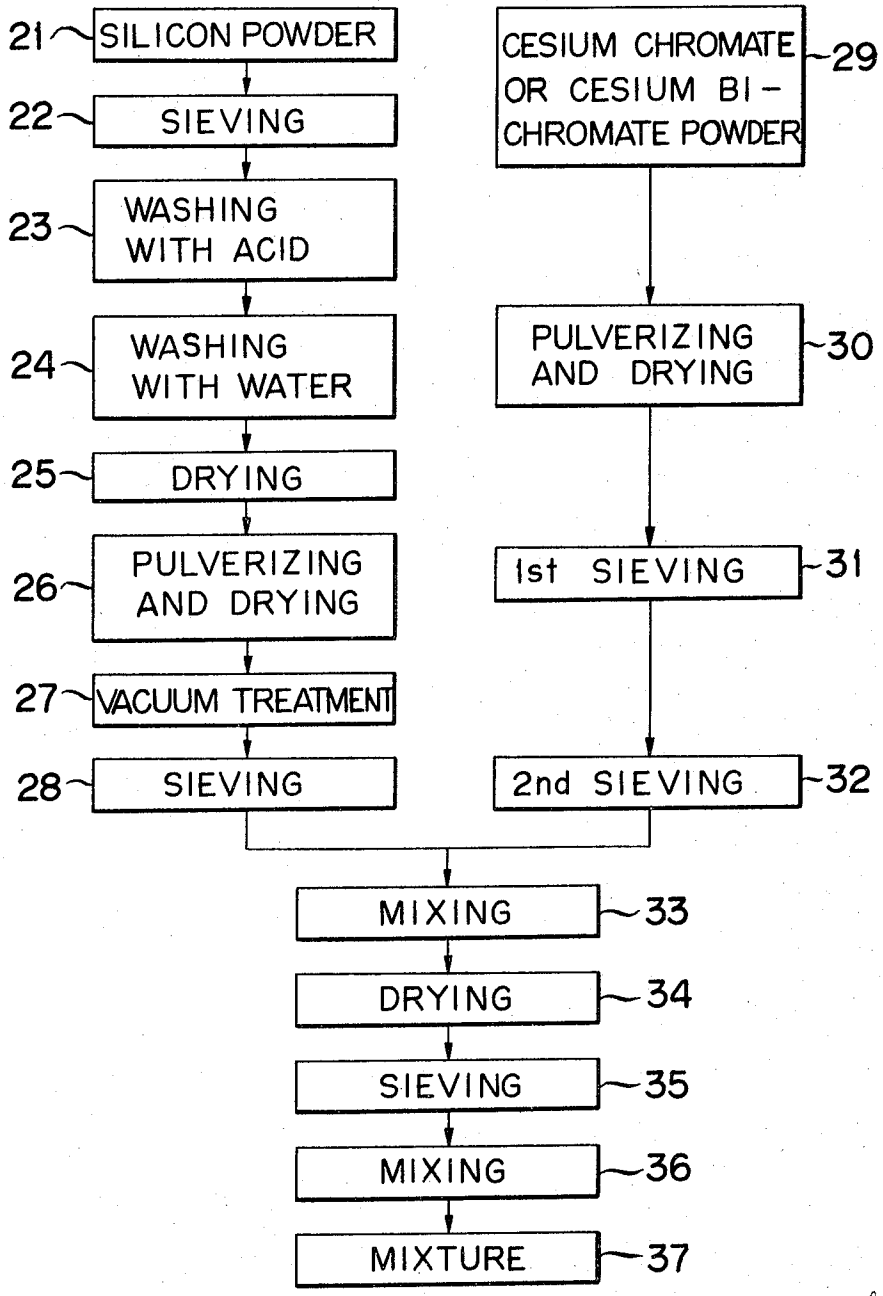


FIG. 7



Haruo Takashio
Takayoshi Matsuzawa
INVENTORS
BY Georges Urjanik
Attorney

FIG. 8



Haruo Takeshita
Takeyoshi Matsuzawa

BY

INVENTORS

George B. Cenzorelli
Attorney

CESIUM EVAPORATOR

The present invention relates to a cesium evaporator for depositing cesium vapor on the face plate of a photoelectric tube, and more particularly to a cesium evaporator capable of evaporating cesium at a constant rate.

In depositing cesium vapor on the face plate of a photoelectric tube, it is generally the practice to use an evaporator having a lead wire fitted to each end and filled with a mixed powder of an appropriate reducing agent and cesium chromate and/or cesium bichromate. Disposed at a suitable distance from the face plate of the photoelectric tube, the cesium evaporator then is electrically heated through the lead wires to produce the vapor of reduced cesium. The vapor of cesium thus produced is emitted through the holes provided on the sidewall of the evaporator and is deposited on a thin layer, for example, of antimony or silver-bismuth already coated on the face plate of the photoelectric tube. It is well known that face plate of high photosensitivity can be obtained only when the face plate is such that the face plate does not display its photosensitivity until a layer of cesium is deposited on the face plate preliminary coated with a metal base such as antimony or silver-bismuth.

To prepare in good yield a face plate of uniform high photosensitivity, it is required that the volume of cesium vapor generated by the evaporator, composition of the reactants present therein and velocity of cesium deposition on the metal base per unit time are perfectly constant until completion of said deposition. However, in the prior art, the cesium evaporator is filled indiscriminately with mixed powders of cesium chromate and/or cesium bichromate and at least one element selected from the group consisting of such reducing agents as zirconium, iron, calcium, tungsten, silicon, aluminum and titanium, and sufficient attention is not given to particle size distribution of these powders, absorption of water and/or gas thereto, and surface conditions of the powder particles. For example, the average particle size of the powders to be mixed is not fully regulated, and there is included a large amount of relatively smaller or larger particles. This leads to varying contact areas among the powder particles filled into the evaporator, causing an uneven reaction velocity. Further, deposition of water on the particles in turn causes their mutual adsorption or agglomeration, thus resulting in nonuniform fluidity and diffusion velocity of powders. Also the adsorption of gases or presence of oxides causes the evaporation of reaction products other than cesium and hinders the production of cesium vapor. As a result, it has been impossible to regulate the reaction velocity and the evaporator itself sometimes tends to be damaged by an abrupt reaction. Therefore the prior art evaporator was handicapped by various drawbacks as listed above. Use of such cesium evaporator presents difficulties in controlling the reaction velocity, thus affecting the properties of the face plate and of the secondary electron-multiplying electrode which the resultant decline in the yield rate of a photoelectric tube.

The present invention has been accomplished with the view of providing a uniform deposition of cesium vapor on the face plate of a photoelectric tube. The invention provides a cesium evaporator packed with a mixture of silicon powder 30 to 80 microns in the average particle size and substantially free from water and adsorbed gases, the particle size distribution thereof being such that larger particles than 100 microns and those smaller than 1 micron respectively account for not more than 30 weight percent, and powder of cesium chromate and/or cesium bichromate 3 to 10 microns in the average particle size and substantially free from water, the particle size distribution thereof being such that larger particles than 25 microns represent not more than 30 weight percent, and those smaller than 0.5 micron constitute not more than 40 weight percent.

The present invention can be more fully understood from the following detailed description taken in connection with the accompanying drawings in which:

FIG. 1 is a perspective view of a cesium evaporator in common use;

FIG. 2 is a longitudinal section on line II—II of the cesium evaporator shown in FIG. 1;

FIGS. 3 and 4 are curve diagrams showing the relations between the particle size distribution of cesium chromate powder and the yield rate of good quality face plates;

FIGS. 5 to 7 are curve diagrams showing the relations between the particle size distribution of silicon powder and the yield rate of good quality face plates; and

FIG. 8 is a block diagram of the process of obtaining a mixture of desired powders of silicon, cesium chromate and/or cesium bichromate according to an embodiment of the present invention.

The present inventors have found that when the particle size distributions of silicon powder, cesium chromate and/or cesium bichromate are properly adjusted, and freed substantially of adsorbed water with careful attention given to improving the surface condition of the silicon particles and jointly introduced into an evaporator, the fluidity and contact condition of powders and the diffusion velocity thereof at the time of reaction will become more constant, assuring a greater uniformity in the velocity of cesium vapor deposition on the face plate than has been possible with the prior art method.

There will now be described the process of the present invention by reference to the appended drawings. As shown in FIGS. 1 and 2, an evaporator 11 consists of a cylindrical body 12 made of a thin metal sheet and filled with a mixture 13 of powder of cesium chromate and/or cesium bichromate and that of silicon, both ends of the cylindrical body being pressure-sealed, and fitted with a pair of lead wires 14, 14. The overlapped portion of the thin metal sheet 12 is joined together by equally spaced welds 15 . . ., forming between them a plurality of holes 16 . . . to allow the cesium vapor produced in the evaporator 11 easily to scatter therefrom.

The present invention utilizes an evaporator of the same construction as described above. However, the powder of cesium chromate or cesium bichromate charged into the evaporator 11 has such a particle size distribution that the average particle size ranges between 3 and 10 microns and that larger particles than 25 microns constitute not more than 30 weight percent and those smaller than 0.5 micron account for not more than 40 weight percent. If the powder of cesium chromate or cesium bichromate has a smaller average particle size than 3 microns it tends to agglomerate in itself with the resultant poor dispersion in the silicon powder with which it is to be mixed. This will generally cause the cesium compounds to react with silicon rapidly and irregularly. On the other hand, where the particle size of powdered cesium compounds exceeds 10 microns, reaction with silicon will sharply rise when the reaction proceeds to a certain interim stage, though substantially slow in the initial period, due to the smaller surface area of these particles. In the worst case the evaporator will be damaged by an abrupt reaction.

Further, even though the average particle size may fall within the range of from 3 to 10 microns, if the powder of cesium compounds contains more than 30 weight percent of particles smaller than 0.5 micron, the reaction velocity will not be constant due to the absence of uniform contacts between the cesium compounds and silicon. Therefore, as shown in both FIGS. 3 and 4, the yield rate of good quality face plates (namely, the ratio of good quality product to the total output) will sharply decline. In FIG. 3 the ordinate represents the yield rate of good quality face plates and the abscissa the weight percent of smaller particles than 0.5 micron included in the cesium chromate powder of 3 to 10 microns in the average particle size. In FIG. 4, the ordinate denotes the yield rate of good quality face plates and the abscissa the weight percent of larger particles than 25 microns included in the cesium chromate powder 3 to 10 microns in the average particle size. These tendencies shown in FIGS. 3 and 4 are also true with the cesium bichromate powder. The term "good quality product," as used in this specification, is defined to mean the face plate wherein the amount of cesium vapor deposited in the aforementioned manner on the face plate by introducing a

prescribed quantity of electric current through the evaporator falls in the range of 30 to 50 percent of the stoichiometrical value to be produced by the reaction of cesium chromate or cesium bichromate with silicon. Accordingly, the 100 percent production of good quality face plates represents that the cesium vapor is deposited on the face plate at a perfectly uniform velocity. The particle sizes appearing throughout this application have been measured by means of micromerograph.

The silicon powder used in the process of the present invention has such a particle size distribution that the average particle size ranges between 30 and 80 microns and that those larger than 100 microns or those smaller than 1 micron respectively account for not more than 30 weight percent. The silicon powder of less than 30 microns in the average particle size is undesirable in that the surface of the particles is vulnerable to oxidation. Conversely, where the average particle size exceeds 80 microns, the surface area of each particle will be reduced relative to the volume thereof. Therefore, when the powder of cesium chromate or cesium bichromate having a far smaller average particle size is mixed with such large silicon particles, there will not be obtained a satisfactory contact between these two kinds of powders. For example, where, as shown in FIG. 5, the average particle size of silicon powder falls outside of the range of from 30 to 80 microns, the yield rate of good quality face plates is significantly reduced. In FIG. 5, the ordinate represents the yield rate of good quality face plates and the abscissa the average particle size (micron) of silicon powder. If the silicon powder contains more than 30 weight percent of particles larger than 100 microns and smaller than 1 micron respectively, even though the average particle size may fall within the range of from 30 to 80 microns, these silicon particles will not have a uniform contact with those of cesium chromate or cesium bichromate. The employment of such silicon powder leads to an uneven reaction velocity of cesium evaporator and sharply reduces, as shown in FIGS. 6 and 7, the yield rate of good quality face plates. In FIG. 6 the ordinate denotes the yield rate of good quality face plates and the abscissa the weight percent of larger particles than 100 microns included in the silicon powder 30 to 80 microns in the average particle size. In FIG. 7, the ordinate represents the yield rate of good quality face plates and the abscissa the weight percent of smaller particles than 1 micron contained in the silicon powder 30 to 80 microns in the average particle size.

Not less important for the process of the present invention is the substantial elimination of adsorbed water, in addition to the aforementioned control of particle size distribution of powders of cesium compounds and silicon. Particularly with respect to the silicon powder, it is preferable to reduce adsorbed gases as much as possible by vacuum heating after pulverizing and drying. Regarding the powder of cesium chromate or cesium bichromate, it is also advisable to repeat several times the cycle of pulverizing and drying so as to obtain water-free powder having prescribed average particle size and particle size distribution and thereafter sieve them using two screens of different mesh sizes to prevent the agglomeration of very fine particles. Specifically, this sieving is preferably carried out first with a coarse screen, for example, of 60 Tyler mesh, and then with a finer screen, for example, of 200 Tyler mesh. If a fine screen is used from the start, then even agglomerated minute particles will be pressed down and forced out through the mesh. Therefore, the aforementioned two-step sieving with a coarse and a fine screen is effective to prevent such occurrence. To prevent the adsorption of moisture, the entire cycle of sieving is preferably carried out under the irradiation of an incandescent lamp or infrared-ray lamp.

The silicon powders processed to have a prescribed particle size distribution and surface condition by washing with acid and water, drying, vacuum treatment and sieving are mixed in a mixer with powders of cesium chromate and/or cesium bichromate similarly subjected to the aforesaid two-step sieving in such a manner that these powders may not be pulverized. The mixed powder is further dried and sieved to prevent the agglomeration of the powder. If required these mixing, drying, and sieving steps may be conducted in a vacuum vessel.

The mixed powder thus treated is satisfactory in respect of the particle size, adsorbed water and gases and mutual contact, so that the resultant fluidity, reaction area and diffusion velocity thereof become constant, thus enabling cesium vapor to be uniformly deposited on a thin film of silver-bismuth or antimony constituting the metal base of the face plate. Therefore the evaporator charged with such a mixed powder displays very excellent effects, for example, unfailingly depositing a prescribed amount of cesium vapor, and significantly improving the properties of the face plate and the yield rate of photoelectric tubes.

There will now be described the method of depositing cesium vapors according to an embodiment of the present invention.

2,500 g. of 99.9 percent pure silicon powder having a nearly uniform particle shape was sieved with a 200 Tyler mesh screen. 500 g. of the powder thus sieved was washed with a solution of 10 percent hydrochloric acid, and then completely stripped of the deposited hydrochloric acid with distilled water. This portion of the power was dried 60 minutes in a thermostatically controlled oven maintained at a temperature of 100° C., and was introduced into a 200 ml. stainless steel pot together with 50 stainless steel balls, and repetitively subjected to eight cycles of 30 minutes pulverizing treatment by rotating the pot at a velocity of 100 r.p.m. Between these pulverizing treatment was introduced a drying step of 10 minutes in a thermostatically controlled oven maintained at 100° C. The silicon powder thus treated was measured to have an average particle size of 60 microns, larger particles than 100 microns accounting for 15 weight percent and those smaller than 1 micron, 20 weight percent. The silicon powder having such particle size distribution was introduced into a suitable vessel placed in a vacuum region. When evacuation was carried out and the vacuum region reached a vacuum of 3×10^{-5} torr, heating was applied for degassing 1 hour at 850° C. using an electric heater with the pressure within the aforesaid vessel maintained within the range of from 3×10^{-5} to 9×10^{-5} torr. Upon completion of heating, the powder was allowed to cool 3 hours under vacuum. Next, while projecting light beams from an infrared-ray lamp, the powder was allowed to pass through a 150 Tyler mesh screen.

At the same time, cesium chromate powder was repeatedly subjected to pulverizing and drying as in the case of silicon powder until the cesium chromate powder had an average particle size of 6 microns and particles larger than 25 microns accounted for 8 weight percent and those smaller than 0.5 micron represented 0.4 weight percent. The powder was sieved under the irradiation of an incandescent lamp in two steps first with a 60 Tyler mesh screen and then with a 120 Tyler mesh screen.

Two parts by weight of the silicon powder and 1 part by weight of cesium chromate powder thus obtained were introduced into a V-type mixer and mixed at a velocity of 50 r.p.m. without substantially pulverizing these two kinds of powders. The mixing operation was intermittently conducted over a total period of 3 hours by introducing between the operations a drying step of 30 minutes at 100° C. and a sieving step with a 60 Tyler mesh screen under the irradiation of an infrared-ray lamp.

The above processes may be schematically represented as shown in FIG. 8. Namely, silicon powder **21** was processed in the order of sieving **22**, washing with acid **23**, washing with water **24**, drying **25**, several times of pulverizing and drying **26**, vacuum treatment **27** and sieving **28**, while cesium chromate **29** was processed in the order of several times of pulverizing and drying **30**, the first sieving by coarse screen **31** and the second sieving by fine screen **32**. This was followed by mixing process **33**, drying **34**, sieving **35** and mixing process **36**. If required the processes of **33**, **34**, **35** and **36** may further be repeated to finally obtain the mixture **37**.

The evaporator of FIG. 1 filled with the mixed powder thus treated was electrically heated to deposit cesium vapor on the face plate of a photoelectric tube, the yield rate of good quality face plates being 98 to 100 percent. Another experiment was carried out under the same conditions as in the foregoing example, excepting that the cesium chromate used in said example was replaced by cesium bichromate. In this case there were also obtained substantially the same results. By way of comparison, the deposition of cesium vapor was carried out by employing a mixture which was omitted of the intermediate steps of drying the raw powders, heating the silicon powder under vacuum and sieving the cesium chromate powder in two stages between the respective cycles of the aforementioned pulverizing operation. In this case, the yield rate of good quality face plates sharply declined to 40 to 95 percent.

While the invention has been described in connection with some preferred embodiments thereof, the invention is not limited thereto and includes any modifications and alternations which fall within the scope of the invention as defined in the appended claims.

What is claimed is:

1. A method for preparing a source for generating cesium vapor from which cesium is evaporated at a constant rate which comprises:

1. preparing a silicon powder having a particle size distribution such that the average particle size is between 30 and 80 microns and in which particles larger than 100 microns constitute not more than 30 weight percent of the mixture and particles smaller than 1 micron constitute not more than 30 weight percent of the mixture by repeatedly pulverizing and drying said silicon powder until a mixture with the stated particle size distribution is obtained;

degassing and removing any adsorbed moisture from the resulting powder by subjecting the powder to a vacuum;

and then sieving said dried, degassed powder;

2. preparing a powder of at least one cesium compound selected from the group consisting of cesium chromate and cesium bichromate, said powder having a particle size distribution such that the average particle size ranges between 3 and 10 microns and not more than 30 percent of the mixture by weight consists of particles larger than 25 microns and not more than 40 percent of the mixture by weight consists of particles smaller than 0.5 micron, by repeatedly pulverizing and drying said cesium compound powder until a mixture having the stated particle size distribution is obtained;

subjecting said powder to a first sieving operation through a relatively coarse mesh screen to break up any large aggregates of powder in said mixture;

and then subjecting said screened powder to a second sieving operation through a relatively fine screen;

3. mixing the silicon powder obtained in (1) with the cesium compound powder obtained in (2) to form a mixture consisting of said silicon powder and said cesium compound powder; and

4. drying and sieving the mixture so obtained to produce a mixture from which cesium is evaporated at a uniform rate.

* * * * *