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METHOD OF MAKING A MULTI-ALKALI CATHODE

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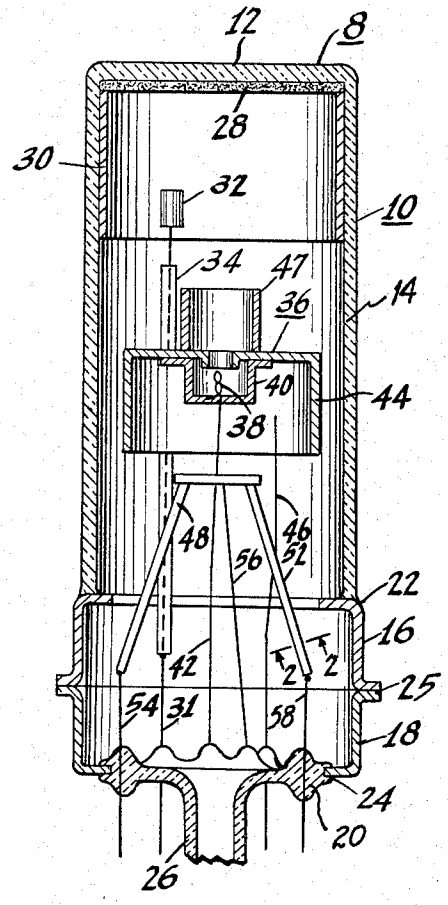


Fig. 1.

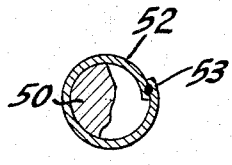


Fig. 2.

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METHOD OF MAKING A MULTI-ALKALI CATHODE

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ABSTRACT OF THE DISCLOSURE

A multi-alkali photocathode including antimony, potassium, sodium and cesium is made by co-evaporating potassium and sodium from a common channel and sequentially evaporating antimony and cesium from two other channels. Substantially the same temperature, i.e., from 160° C. to 175° C., is preserved during the co-evaporation of potassium and sodium and the evaporation of cesium.

My invention relates to the art of making a sensing cathode for image and conversion tubes and particularly to an improved method of making a multi-alkali photocathode.

One type of sensing cathode having a relatively high quantum efficiency and broad spectral response comprises sodium, potassium, antimony and cesium. Several problems are involved in prior methods of making this type of sensing cathode.

One problem concerns the necessity to establish empirically the peak sensitivity at each of a plurality of complex steps. Thus, after an initial antimony layer is deposited on a substrate, the antimony is exposed to potassium vapors until a first peak sensitivity is obtained. Thereafter sodium is evaporated over the potassium until a second and higher peak sensitivity value is obtained. Then antimony and potassium are evaporated alternately until a third and still higher photosensitivity is secured. Thereafter cesium and antimony are alternately evaporated until a fourth and still higher sensitivity is obtained. The foregoing steps are carried out at temperatures of 160° C. and 220° C. Finally, the coated substrate is cooled gradually to room temperature and at the same time additional antimony and cesium are added by evaporation primarily to preserve the aforementioned fourth peak sensitivity during the cooling period.

In securing the third peak sensitivity as by alternately evaporating antimony and potassium, from 2 to 20 or more antimony-potassium alternations are required. The same is true with respect to the cesium-antimony evaporations for securing the fourth peak sensitivity. Not only are these steps time consuming and require highly skilled operators, but they introduce relatively large variations in sensitivity from cathode to cathode. Furthermore, the multiple evaporations of antimony are found to lack uniformity from cathode to cathode so that the cathodes produced are of varing thickness. Such variation in thickness is accompanied by undesired variations in the spectral response.

Another problem concerns the number of evaporators required in the tube envelope by prior practices. Each of the evaporations referred to is performed in the tube envelope after evacuation thereof or while undergoing evacuation. Therefore, an evaporator, usually in the form of an elongated channel is required for each of three of the materials employed in forming or activating the cathode. An evaporator channel is not required for the antimony generation since such generation is effected by heating a filament that has a coating of antimony alloy thereon. The three evaporator boats as well as the filament from which antimony is generated, must remain in

the tube after processing. These elements require a relatively large space and thus can be used only in a tube having a relatively large envelope. Tubes having envelopes of a size too small to tolerate the three evaporators and filament are thus precluded from having the highly desirable multi-alkali photocathode aforementioned.

An object of my invention is to provide an improved method of making a multi-alkali photocathode.

Another object is to provide a more readily reproducible method of making a multi-alkali photocathode.

A further object is to provide a method of making a multi-alkali photocathode with a reduced number of evaporators.

In accordance with my improved method, multi-alkali photocathodes may be made in accordance with a standard that assures uniformity in the sensitivity of a plurality of photocathodes. Such uniformity in sensitivity is achieved by simplifying the steps required for determining peak sensitivities. Simplification is attained by appreciably reducing the number of evaporating steps and thereby assuring improved control with respect to sensitivity. This desirable reduction in the number of evaporating steps is made possible by my discovery of optimum temperatures to be employed in carrying out the several steps, and as a consequence of my finding that two of the alkalis required for a multi-alkali cathode can be co-evaporated effectively from a single evaporator boat.

In practicing my method the number of alternate evaporations characteristic of prior methods are avoided. Maximum sensitivity is determined at each of several steps in practicing my method, by varying the added amount of only one of the ingredients of the photocathode. The absence of control of the prior alternate evaporations is therefore avoided. In addition, the co-evaporation of two of the alkalis from a single evaporator boat avoids crowding the interior of a tube envelope and extends the use of the desirable multi-alkali cathode to tubes that could not accommodate the number of evaporators required heretofore.

Further objects and features of the subject-matter disclosed will become apparent as the present description continues.

In the drawing, which shows an example of a phototube in connection with which my novel method may be practiced:

FIG. 1 is a longitudinal section, by way of example, of a phototube having therein a reduced number of evaporators for making a multi-alkali photocathode; and

FIG. 2 is an enlarged sectional view taken along the line 2—2 of FIG. 1.

The phototube **8** shown in FIG. 1, in connection with which my invention may be practiced, comprises an envelope **10** having an end wall or faceplate **12**. The envelope **10** includes a glass portion **14** integral with the faceplate **12**. The envelope also includes two metal sealing flanges **16**, **18** and a glass stem **20**. The glass of envelope portion **14** and stem **20** may be of different composition. For example, the glass of envelope portion **14** may be a type that seals best to a chrome-iron alloy consisting by weight for example of 27% chromium and 73% iron by weight. Accordingly, the flange **16** may be made of this alloy. The glass of stem **20** may be a type that seals best to an alloy known under the trade name of Kovar and consisting by weight of 53% iron, 18% cobalt and 29% nickel. The sealing flange **18** may be made of this alloy. These combinations of glass and metal result in good vacuum tight glass-to-metal seals **22** and **24**. The metal flanges **16**, **18** may be joined to each other at a region **25** as by heliarc welding to form a hermetic closure. A glass exhaust tubulation **26** per-

mits evacuation of the tube envelope as by connection to suitable pumps (not shown) during a practice of my method. After the steps of my method have been completed, the tubulation 26 may be hermetically closed as by a pinch-off (not shown).

A photocathode 28 formed on the inner wall of the faceplate 12 by my improved method, comprises antimony, potassium, sodium and cesium. The photocathode 28 may have a thickness of several hundred Angstroms. A portion of the inner wall of glass portion 14 of the tube envelope has a coating 30 of aluminum thereon about 0.1 micron thick. The aluminum coating 30 extends into electrical contact with photocathode 28. A lead in conductor 31 hermetically sealed through the stem 20 supports a metal contact tab 32 at its upper end. The conductor 31 is made of stiff wire material such as 0.030 inch diameter stainless steel so as to cause the tab to bear against the aluminum coating 30 for good electrical contact therewith. The conductor 31 has a glass sleeve 34 shrunk thereon to avoid arcs between the conductor 31 and other elements to be described, operated at an appreciable voltage difference.

One element operated at a relatively high voltage with respect to the coating 30 is an anode structure 36. The anode structure includes an antimony generator in the form of a coating of antimony alloy on a filament 38. The filament 38 has one leg thereof connected to an open-ended metallic shield 40 and the other leg to a lead-in conductor 42 sealed to the stem 20. The shield 40 is mounted on and in electrical contact with a further shielding structure of the anode 36 having a skirt 44. A lead-in conductor 46 is electrically connected to the skirt 44. Thus, a connection of lead-in conductors 42, 46 across a suitable electrical current supply, provides energy for heating the filament 38 to a temperature for evaporating the antimony thereon. A further shield 47 serves to direct the evaporated antimony to the faceplate 12.

Within the envelope 10 are disposed sources of potassium, sodium and cesium. The cesium source comprises an intimate mixture of cesium chromate, zirconium and tungsten powder contained within a channel 48 made of tantalum for example. A combined source of potassium and sodium in the form of a suitable mixture or charge 50 (FIG. 2) is contained within a channel 52 also made of tantalum for example and similar to channel 48. Each of the channels 48, 52 includes an overlap region 53 as shown in FIG. 2. The two overlapping portions of the channels are spot welded at spaced portions of the overlap. The portions of the overlap between the spot welds respond in opening or rupture to pressures within the channels produced during a heating thereof, as will be described. Such rupture releases vapors of sodium and potassium from channel 52 and cesium vapor from channel 48. The wall thickness of each of the channels referred to may be about 1 mil and the length may be about 40 mm., to facilitate heating thereof by I^2R losses therein. Such heating of channel 48 may be effected by connecting lead-in conductors 54, 56 to a suitable electrical current supply. Desired heating of channel 52 may be accomplished by connecting lead-in conductors 56 and 58 across an appropriate current supply. It will be noted that this arrangement permits independent heating of the channels 48, 45 with attendent independence in evaporating the charges in the two channels.

The mixture 50 provided for co-evaporating potassium and sodium, in one example, contains the following materials by weight: 45% zirconium, 7% potassium chromate (K_2CrO_4), 7.5% hydrated sodium tungstate ($Na_2WO_4 \cdot 2H_2O$), and 40.5% tungsten. In other examples where it is desired to change the proportions of sodium and potassium vapors produced: the amount of potassium chromate is maintained fixed; the amount of sodium tungstate is varied from 1 to 15%; and the tungsten is varied from 33 to 47%. There materials are

mixed in powder form of relatively small powder size so as to pass through an 80 mesh sieve to provide the charge 50. In one example, the amount of this mixture placed in trough 52 is about 90 milligrams.

The amounts of sodium and potassium in this mixture are determined empirically to provide a ratio of two mol parts sodium to one mol part potassium in the completed photocathode. This results in the desired Na_2K formulation believed necessary for a good multi-alkali photocathode. The amounts indicated include an empirically determined excess of potassium over that needed for a desired photocathode, in order to compensate for the preferential evaporation of potassium resulting from the fact that it has a higher vapor pressure than sodium. The zirconium and tungsten in the mixture serve as reducing agent and inhibitor, respectively, for liberating potassium and sodium from the compounds in which they are included.

One example of a practice of my novel method comprises the following steps. The photocathode 8, shown in FIG. 1, prior to forming the photocathode 28 and before tip-off of the exhaust tubulation 26, is sealed to a glass tubulation of a mercury diffusion pump manifold (not shown). The enevlope of the diode is evacuated to a pressure of about 10^{-6} torr. While connected to the exhaust system, the phototube 8 is baked at a temperature of about 400° C. for about one hour, as by being placed in a suitable oven (not shown). This bake while under exhaust serves to drive out occluded gases from the components of the diode. The photodiode 8 is then cooled to room temperature, i.e., about 27° C.

While at room temperature, the filament 38 is energized by connecting lead-in conductors 42, 46 across an electrical current supply of about 3.5 amperes. Such energization of the filament 38 causes antimony from an antimony-platinum alloy containing by weight 40% antimony and 60% platinum coated on the filament, to vaporize and be directed by shield 47 to the faceplate 12. The antimony evaporation is continued until light transmission through the faceplate 12 is reduced to 65%.

The diode envelope is then raised to a relatively high temperature of 165° C. with tolerable variation from 160 to 175° C. This temperature of the diode 8 is preserved during the several steps of evaporating potassium, sodium and cesium to be described.

The channel 52 containing the potassium-sodium charge 50 is then heated by connecting lead-in conductors 56, 58 to a source of electrical current. The magnitude of the electrical current is gradually increased from 3 amperes to 4.8 amperes, in steps each having a time duration found best empirically for sensitivity of the resultant photocathode as will appear in the following.

In order to produce the formulation Na_2KSb in forming the multi-alkali cathode 28, it is believed necessary that the mol ratio of sodium to potassium be 2 to 1 for best results. However, the vapor produced by heating the potassium-sodium charge 50 must have potassium in an amount in excess of that required by the foregoing ratio. This is because it is necessary to compensate for the difference in reaction rate and the difference in speed at which the sodium and potassium are lost by being pumped from the envelope 8 through the tubulation 26. This excess amount of potassium which is provided in the formulation of the charge 50 as described before herein, will allow the formation of Na_2KSb. The particular mixture used, as described before herein, has been determined empirically and has been found to provide the compensation aforementioned as well as the relative amounts of sodium and and potassium vapors necessary for the highest stable value of photocurrent which it is believed can be realized from a photocathode compresing Na_2KSb.

The actual heating schedule referred to in the foregoing to which the potassium-sodium containing channel 52 is subjected, is determined by the following empirically de-

termined stepped values of heating current and time duration of each step:

Heating current in amperes:	Time in minutes
3.0	2
3.5	3
4.0	1
4.4	4
4.5	1
4.6	1
4.8	2

Heating of the channel **52** and further evaporation of the charge **50** therein is then terminated. The photocurrent from the diode **8** assumes a stable value of about 0.75 microampere per lumen. The diode **8** is then baked at the temperature of the diode envelope, i.e., about 165° C., for about 65 minutes without evolution of any alkali from the channels **48**, **52** or of any antimony from the filament **38**. After this period of bake the sensitivity of the partly-formed photocathode **28** increases about threefold to a stable value of about 2.5 microamperes per lumen. The sodium-potassium containing channel **52** is then heated again by an electric current source of 4.8 amperes. This causes a rapid increase in sensitivity to take place to 22.5 microamperes per lumen. Further independent heating of the channel **52** is then stopped.

Thereafter, the cesium-containing channel **48** is heated in steps by connection to a variable source of electrical current. The amount of current used at each step, as well as the duration of each step, is determined empirically for maximum sensitivity. The schedule found best is as follows:

Current in amperes:	Time of duration in minutes
3.0	½
3.5	1
4.0	1
4.5	½

The yield of cesium during a practice of this schedule has an erratic effect on sensitivity. Thus, during the first three steps, the sensitivity may decrease from 22.5 microamps per lumen to 17 microamps per lumen. During the final step, the sensitivity may first increase from 17 microamperes per lumen to 29 microamperes per lumen and then decrease rapidly to 7.5 microamperes per lumen.

When this schedule is completed, current energization of the cesium containing channel **48** is stopped. An immediate rise in sensitivity of from 7.5 microamperes per lumen to about 50 microamperes per lumen is noted after energization of channel **48** is stopped. The diode **8** is exposed to the bake temperature hereinbefore referred to, i.e., about 165° C., for about 10 minutes after completion of the aforementioned schedule. During such bake period, a steady increase in the sensitivity of the photocathode **28** occurs from about 50 microamperes per lumen to about 90 microamperes per lumen.

A further increase in sensitivity of the photocathode **28** is evidenced during a subsequent cooling of the diode. It is found empirically that for best results the cooling should be effected in steps of different cooling rates. A cooling schedule resulting in an increase in sensitivity of from about 90 microamperes per lumen to about 140 microamperes per lumen is as follows:

Temperature drop, degrees C.	Cooling rate, degrees C./min.
167–133	2.8
133–103	2.2
103–79	1.3
79–56	0.8

56–38	0.4
38–27	0.2

The aforedescribed different cooling rates are effected by gradually removing the diode from the baking oven. The time period involved is about two and one-half hours.

The final step in making the photodiode **8** involves hermetically closing the exhaust tubulation **26** as by a suitable tip-off.

What is claimed is:

1. Method of making a multi-alkali photocathode comprising:

(a) first evaporating a layer of antimony on an insulating substrate,

(b) then co-evaporating sodium and potassium from a common source over said antimony substrate, and then

(c) evaporating cesium over said sodium and potassium.

2. Method of forming a multi-alkali photocathode on a transparent insulating wall of a tube envelope comprising:

(a) continuously evacuating said envelope,

(b) first evaporating a layer of antimony on said wall at substantially room temperature,

(c) thereafter heating said envelope to a temperature of from 160° C. to 175° C.,

(d) co-evaporating sodium and potassium from a common charge including sodium and potassium in a mol ratio in which the potassium yield is in excess of one-half the yield of sodium, while said envelope is heated at said temperature, to provide a deposit on said antimony layer of sodium and potassium in the mol ratio of 2 to 1,

(e) evaporating cesium on said deposit of sodium and potassium while said envelope is at said temperature, and

(f) gradually cooling said envelope to room temperature.

3. Method of forming a multi-alkali photocathode according to claim **2** and including the steps of:

(a) confining within a pressure rupturable channel a charge adapted to yield sodium and potassium vapors in amounts which include an excess of potassium over the mol ratio of 2 parts sodium and 1 part potassium,

(b) heating said channel to produce a pressure therein for rupturing the channel and to release said yield of sodium and potassium vapors, and

(c) evacuating said envelope during said heating of the channel, whereby some of the yield of sodium and potassium vapors are evacuated from said envelope, the mol ratio of the vapors so evacuated being 2 parts of sodium and 1 part of potassium plus said excess.

4. In a reproducible method of making a multi-alkali photocathode consisting of a first evaporation of antimony, a second evaporation of sodium and potassium, and a third evaporation of cesium, the step of:

(a) heating a cesium-containing heat rupturable channel by passing electric current therethrough for about 3 minutes in 4 steps of gradually increasing current increments, from an initial electric current of about 3 amperes during the first step to a final electric current of about 4.5 amperes during the fourth step, the duration of the first and fourth of said steps being about ½ minute each, and the duration of the second and third of said steps being about 1 minute each.

5. In a reproducible method of making a multi-alkali photocathode in a tube envelope and which method includes heating said envelope to a temperature of from 160° C. to 175° C. while evaporating cesium in the tube envelope as a final addition to said photocathode, the step, after evaporation of said cesium, of:

(a) gradually reducing the temperature of said en-

velope from said temperature to room temperature throughout a period of about 2½ hours, at a gradually reduced cooling rate of initially about 2.8° C. per minute from said temperature to a temperature of about 133° C., and finally at a cooling rate of about 0.2° C. per minute from a temperature of about 38° C. to a temperature of about 27° C.

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