United States Patent

Helvy

[15] **3,658,400**

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[54] METHOD OF MAKING A MULTIALKALI PHOTOCATHODE WITH IMPROVED SENSITIVITY TO INFRARED LIGHT AND A PHOTOCATHODE MADE THEREBY

[72] Inventor: **Fred Anderson Helvy**, Lancaster, Pa.

[73] Assignee: **RCA Corporation**

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[52] **U.S. Cl.**.....**313/94**, 117/33.5 CP, 316/5, 316/6, 316/8, 316/10

[51] **Int. Cl.**.....**H01j 39/00**

[58] **Field of Search**.....316/3, 1, 10, 5, 6, 8; 117/33.5 C, 33.5 CP, 219, 217; 313/65 R, 94

[56] **References Cited**

UNITED STATES PATENTS

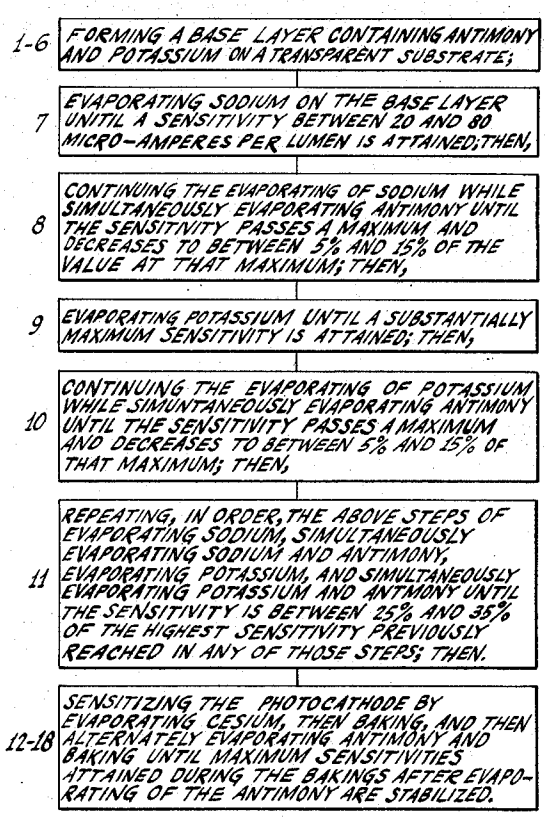
2,431,401	11/1947	Janes	316/6 X
2,770,561	11/1956	Sommer	313/102 X
2,914,690	11/1959	Sommer	117/217 X
3,179,835	4/1965	Kaseman	117/219 X
3,372,967	3/1968	Hughes	316/5
3,498,834	3/1970	Rome et al.	117/217

Primary Examiner—John F. Campbell
Assistant Examiner—Richard Bernard Lazarus
Attorney—Glenn H. Bruestle

[57] **ABSTRACT**

A method for making a multialkali photocathode includes simultaneous evaporation of sodium and antimony alternately with simultaneous evaporation of potassium and antimony. The disclosure includes a photocathode made by the method described.

8 Claims, 3 Drawing Figures



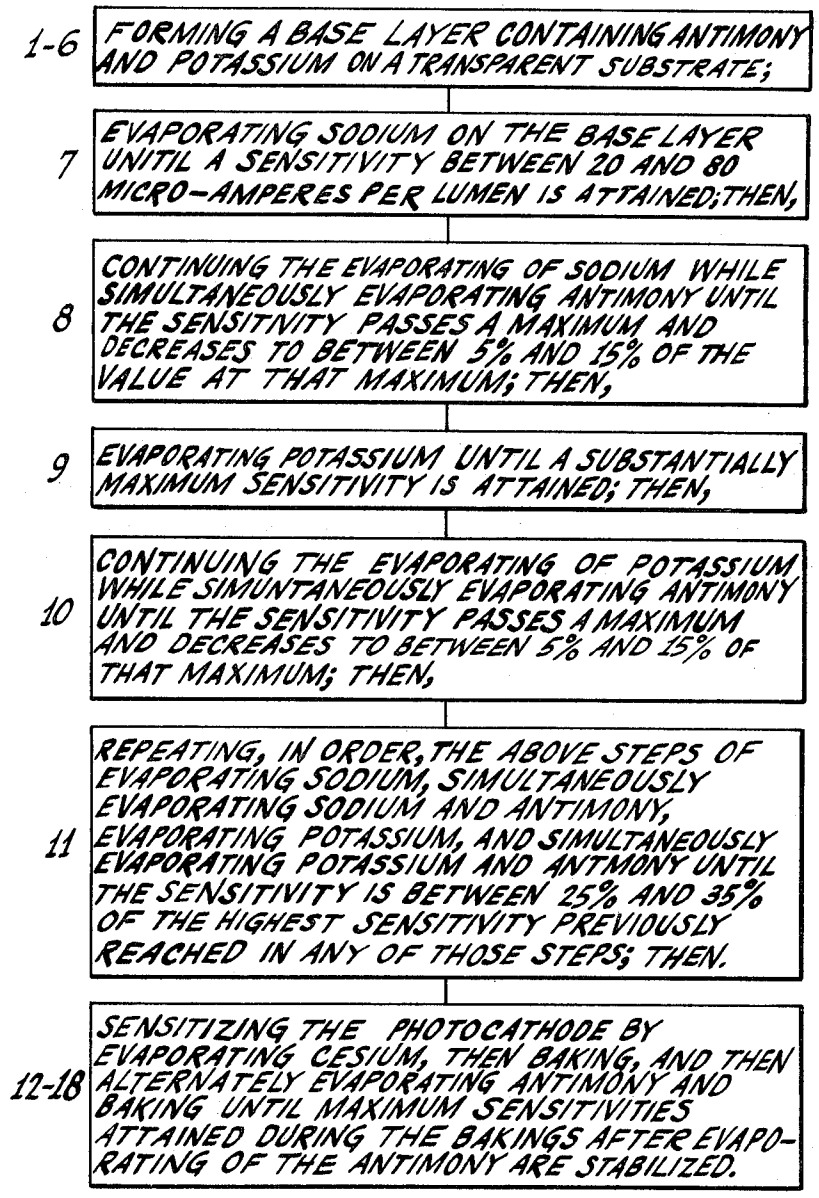


Fig. 1.

INVENTOR.
FRED A. HELVY
BY
Volker R. Ulbrich
Attorney

Fig. 2.

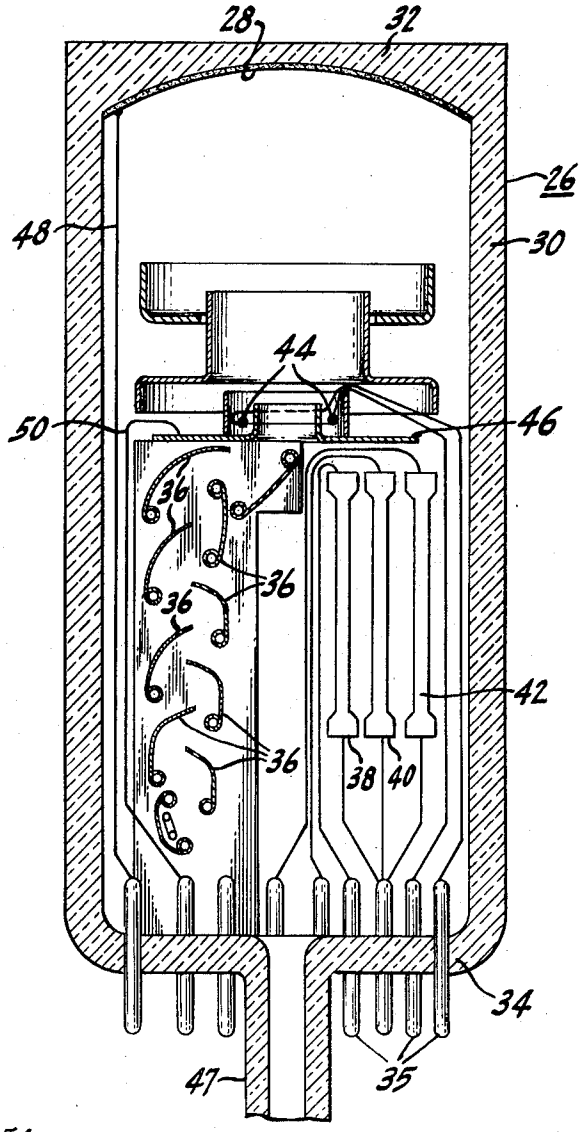
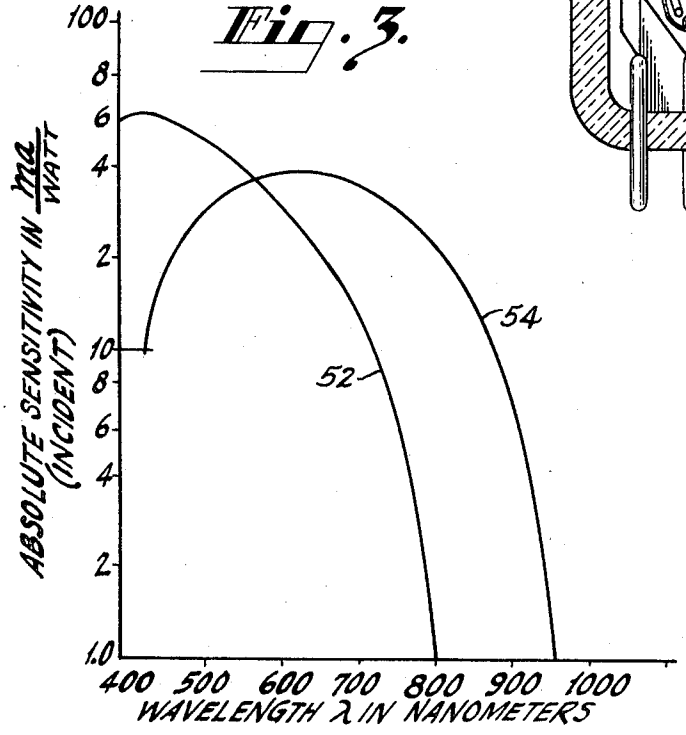


Fig. 3.



INVENTOR.
FRED A. HELVY
BY Volker R. Ulbrich
Attorney

METHOD OF MAKING A MULTIALKALI PHOTOCATHODE WITH IMPROVED SENSITIVITY TO INFRARED LIGHT AND A PHOTOCATHODE MADE THEREBY

BACKGROUND OF THE INVENTION

This invention relates to the art of making photoemitting surfaces. A previous type of photoemitting surface is a semi-transparent, multialkali photocathode such as described, for instance, in U.S. Pat. No. 2,770,561, to A. H. Sommer and No. 3,372,967, to F. R. Hughes. Multialkali photocathodes of this type have a relatively high sensitivity and a spectral response which extends throughout the visible light region of the spectrum.

Previous methods for making multialkali photocathodes require considerable skill on the part of the operator. Thus, reproducibility may be poor, with the result that there may be a substantial variance in the response characteristics of finished surfaces. Moreover, photocathodes made by previous methods have little sensitivity in the infrared region of the spectrum where wavelengths are 700 nanometers and longer. Yet, sensitivity to red and infrared may be very desirable since, for example, many lasers commonly used for communications emit red or infrared light.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a flow chart of a preferred embodiment of the novel method.

FIG. **2** is a sectional view of a phototube having a photocathode made by the method of FIG. **1**.

FIG. **3** is a graph comparing the spectral response of the photocathode of FIG. **2** with the spectral response of a multialkali photocathode made by present methods.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

General Tube Structure and Processing Equipment -

FIG. **1** is a flow chart of steps **1–18** used for practicing a preferred embodiment of the novel method. By the steps **1–18**, a phototube **26**, shown in FIG. **2**, is provided with a photocathode surface **28** having improved sensitivity to infrared light. The tube **26** has a tubular glass wall section **30** about 5 inches long, 2 inches outside diameter and one-sixteenth inch thickness. One end of the wall section **30** is closed by a glass faceplate **32**, which is flat on the outside and concave on the inside with a radius of curvature of about 1.9 inches. The other end of the wall section **30** is closed by a stem **34** having a number of electrical lead-in pins **35**. Along the interior of the tube are spaced a series of dynodes **36**. Near the dynodes **36** are spaced three channels **38, 40, 42** of tantalum foil containing, respectively, substances for evaporating potassium, sodium, and cesium. The potassium channel **38** contains potassium chromate, aluminum, and tungsten. The sodium channel **40** contains sodium chromate, aluminum, and tungsten. The cesium channel **42** contains cesium chromate, zirconium and tungsten. A resistance filament situated near the faceplate has two antimony alloy beads **44** attached to it for evaporating antimony. The channels **38, 40, 42** and the filament **44** are suitably connected by internal leads to electrical current sources through the pins **35** so that they can be activated separately by electrical resistance heating.

Light transmission through the faceplate **32** is monitored by directing light from an incandescent tungsten filament at an angle through the faceplate **32** and wall **30** to a light sensing tube. Photoemissive sensitivity of the interior faceplate surface is monitored by collecting the emitted electrons with one or more of the internal electrodes, such as the electrode **46**. For such collection, the electrode **46** is impressed with a voltage of between 50 and 150 volts positive with respect to the photocathode **28** through a lead **48** going from a lead-in pin **35** to an aluminum coating on the wall **30** and in contact with the photocathode **28** and lead **50** also from a lead-in pin **35** to the electrode **46**. The sensitivity is expressed in terms of microamperes of emitted electron current per lumen of light incident on the photocathode **28**.

During processing, the tube is continuously evacuated through exhausted tubulation **47** in the stem. The tubulation is of about ¼ inch inside diameter and about 2 inches long. It leads directly to a titanium evaporation-ion vacuum pump having a pumping speed of about 250 liters per second.

Processing Steps

Referring now to FIGS. **1** and **2**, processing steps for preparing the photoemissive surface are as follows, with ranges of parameters given in parentheses immediately after a preferred value:

1. The tube is baked for about 5 (4 to 6) hours at about 400° C to clean and degas the interior.
2. After the tube is cooled to room temperature, the filament **44** is heated and antimony is evaporated from it until the light transmission of the faceplate **32** is about 60 percent. The transmission of the faceplate **32** before evaporation is defined as 100 percent.
3. The tube **26** is placed in an oven which has been preheated to about 190° C.
4. While the tube **20** is heating to oven temperature, the channels **38, 40, 42** are preheated to clean and degas them. Then the potassium channel **38** current is set so that the channel will release potassium vapor when the faceplate **32** temperature reaches about 180° C.
5. Potassium is evaporated on the antimony layer until maximum sensitivity is reached. The maximum is generally about 1.5 (1–5) microamperes per lumen.
6. The oven temperature is increased to about **220°** (215°–230°) C and the sodium channel **40** current adjusted so that sodium vapor will be released when the faceplate **32** reaches about 210° (205°–220°) C.
7. Sodium is evaporated until a maximum sensitivity is reached. The maximum is generally about 20 (15–80) microamperes per lumen.
8. Sodium evaporation is continued and antimony is simultaneously evaporated until a maximum sensitivity is passed at about 50 (45–120) microamperes per lumen and sensitivity has decreased to about 10 percent (5–15 percent) of the maximum. Then both evaporations are discontinued.
9. Potassium is evaporated until a maximum sensitivity is reached.
10. Potassium evaporation is continued and antimony is simultaneously evaporated until the sensitivity decreases to about 10 percent (5–15 percent) of the maximum sensitivity in step **9**.
11. Steps **7** through **10** are repeated at least several times until the maximum sensitivity in step **10** is about 30 percent (25–35 percent) of the highest maximum sensitivity reached in any of the previous steps **5** through **10**. The photocathode will take on a light blue hue when the proper sensitivity for this step is reached.
12. The tube **26** is cooled gradually to about 160° (155°–165°) C over a period of about 5 (5–10) minutes.
13. When the temperature reaches about 160° C, cesium is evaporated until the sensitivity passes a maximum and decreases to about 90 percent (70–90 percent) of the maximum.
14. The tube **26** is baked at 160° (155°–165°) C until a new maximum sensitivity is reached.
15. Antimony is evaporated until the sensitivity decreases to about 10 percent (5–15 percent) of the maximum reached in step **14**).
16. The tube is baked at 160° (155°–165°) C until a new maximum sensitivity is reached.
17. Steps **15**) and **16**) are repeated until the maximum sensitivity of step **16**) stabilizes and the infrared sensitivity is between 0.5 and 16 microamperes per lumen.

18. With the photocathode **28** completed, the tube **26** is slowly cooled to room temperature at a rate of about 10° C per minute and removed from the oven. After the exhaust tubulation **47** is sealed off, the tube **26** is operative.

GENERAL CONSIDERATIONS

Techniques for monitoring sensitivity and light transmission during processing as well as for evaporating photocathode materials are further described, for instance in the U.S. Patents to A. H. Sommer and F. R. Hughes, referenced above, and also in U.S. Pat. No. 2,914,690 to A. H. Sommer and No. 2,676,282, to J. J. Polkosky.

Light transmission of the faceplate, for the purpose of monitoring the thickness of the antimony layer, is measured by conventional means. Its measurement is not critical.

Sensitivity of the evaporated layers is measured separately for visible light and infrared light. It is desirable to be able to measure both visible and infrared sensitivity almost simultaneously so that the photocathode may be processed to give a favorable relative value of both sensitivities. For this purpose, two separate incandescent tungsten light sources are used, each about 0.1 lumen in output. The sources are spaced apart a short distance from the faceplate. Interposed between one source and the faceplate is a glass light filter passing infrared light but no visible light. For instance, a filter passing less than 0.025 percent at 750 nanometers wavelength, 20 percent at 900 nanometers and about 90 percent at about 1,250 nanometers is suitable. The sensitivity of the photocathode to both visible and infrared light may be measured separately and almost simultaneously by manual switching from one light source to the other.

The rates of evaporation of the evaporated elements are limited by the speed and accuracy at which the sensitivity can be monitored. A relatively slow evaporation rate makes the monitoring less critical.

Maximum sensitivity is determined from the first derivative of the increasing sensitivity function. The first derivative takes a zero value at the peak of a sensitivity curve. A computer can be used to continually calculate the derivative of the sensitivity function, or a human operator can simply observe a plotted curve of the sensitivity and note when its tangent is horizontal to indicate a peak. However, in the course of an alkali metal evaporation there are often a number of spurious peaks in the sensitivity which are of lower values than a later highest maximum peak. In order to discriminate these spurious peaks from the maximum it is necessary to continue evaporation until the sensitivity has fallen to a value of about 80 percent of the sensitivity at the peak in question. It may then be assumed that the peak was the highest attainable for that evaporation and is therefore a maximum. A reference herein to evaporation of an alkali metal to a "substantially maximum sensitivity" means an evaporation past the maximum to at least 15 percent of the sensitivity at the maximum. Excess alkali metal evaporated after a maximum is reached generally evaporates off again during subsequent baking.

While in the preferred embodiment evaporation was done by heated channels inside the tube, external processing, such as is described in the aforementioned patents, can also be used to practice the novel method. Thus, the novel method can be used to form photocathodes having improved red response in tubes, such as image tubes for which internal processing may not be as useful as external processing because of possible contamination of electrodes.

The novel method results in high reproducibility of photocathodes and is thus particularly well suited for automated fabrication of photocathodes. With present methods, complete automation is not feasible because of a relatively low degree of reproducibility in the absence of a highly skilled operator. Furthermore, by the novel method it takes considerably less time, as much as 50 percent less, to make a multialkali photocathode than by present methods.

Present multialkali photocathodes have a thickness on the order of 30 nanometers, whereas photocathodes made by the novel method may have a thickness on the order of 150 nanometers. The greater thickness accounts in part for an increase in the sensitivity of the photocathode to red light, as shown in FIG. 3. The curve **52** in FIG. 3 represents the approximate response characteristic of a commonly used multialkali photocathode made by present methods. The response is seen to be quite low in the 700 nanometer wavelength region. The curve **54** represents the approximate response characteristic of a photocathode made by the novel method. It is seen that the sensitivity is considerably higher in the 700 nanometer region and extends well beyond that region to as far as 950 nanometers in the infrared region. The high sensitivity in the infrared region is believed to be due to factors other than the photocathode thickness. In addition to the improved infrared response, the photocathode made by the novel method has a more nearly constant and higher sensitivity throughout the visual spectrum than present multialkali photocathodes.

Although the novel photocathode is made by a series of evaporations, it is presently not possible to define precisely the actual finished structure, since there is an alloying of the evaporated substances. The chemical compositions of the various thickness portions of the photocathode are not known. Therefore, the novel photocathode can presently be best described as the product of the novel method.

The novel photocathode may be used as a photoemitter on an opaque substrate or as a secondary electron emitting surface.

I claim:

1. Method of making a photocathode, comprising, in order:

a. forming a base layer containing antimony and potassium on a substrate;

b. evaporating sodium on said base layer until a sensitivity between 20 and 80 micro-amperes per lumen is attained;

c. continuing said evaporating of sodium while simultaneously evaporating antimony until the sensitivity passes a maximum and decreases to between 5 and 15 percent of the value at that maximum;

d. evaporating potassium until a substantially maximum sensitivity is attained;

e. continuing said evaporating of potassium while simultaneously evaporating antimony until the sensitivity passes a maximum and decreases to between 5 and 15 percent of that maximum;

f. repeating, in order, the above steps *b* through *e* until the sensitivity is between 25 and 35 percent of the highest sensitivity previously reached in any of the steps *b* through *e*, and then

g. sensitizing said photocathode by evaporating cesium, baking, and then alternately evaporating antimony and baking until maximum sensitivities attained during said bakings after evaporating of said antimony are stabilized.

2. The method defined in claim **1** and wherein said step a of forming said base layer includes:

i. cleaning and degassing a transparent substrate surface by heating said substrate for at least 3 hours to a temperature of about 400° C in a vacuum;

ii. evaporating an antimony layer on said surface to a thickness which decreases the transmission of yellow visible light through said substrate by at least 5 percent;

iii. heating said surface to at least 150° C;

iv. evaporating a potassium layer on said antimony layer until photoemission from said potassium layer is substantially maximum value.

3. The method defined in claim **1** and wherein said substrate is maintained at a temperature of between 200° and 250° C during said steps *b* through *f*.

4. The method defined in claim **1** and wherein said sensitizing includes:

h. cooling said substrate from the temperature at which said evaporating of potassium is carried out to a temperature

of between 155° and 165° C over a period of between 5 and 10 minutes;

i. evaporating cesium during said cooling until the sensitivity passes a maximum and decreases to between 70 and 90 percent of said maximum;

j. baking said substrate until a new approximately maximum sensitivity is attained;

k. evaporating antimony until the sensitivity decreases to 5 to 60 percent of said maximum sensitivity in step *i*;

l. baking said substrate until a new approximately maximum sensitivity is attained;

m. repeating steps *k* and *l* in order until said maximum sensitivity of step **1** stabilizes to a value of at least 0.1 microampere per lumen for infrared light.

5. An electron emissive photocathode made by the method defined in claim **1**.

6. An electron emissive photocathode made by the method defined in claim **2**.

7. An electron emissive photocathode made by the method defined in claim **3**.

8. An electron emissive photocathode made by the method defined in claim **4**.

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