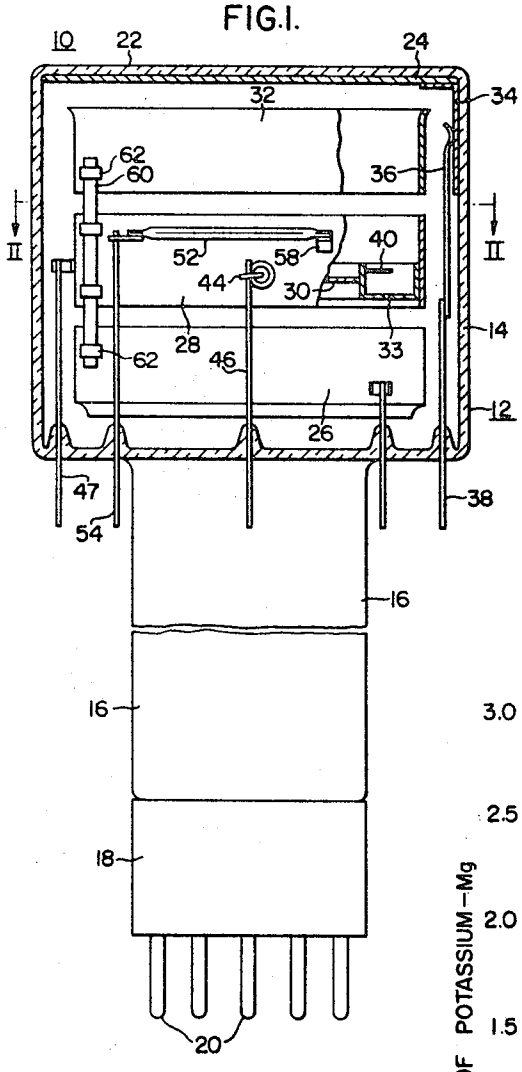
Sept. 23, 1969 C. D. SPANGENBERG 3,468,807

ALKALI METAL GENERATOR

Filed Nov. 19, 1965

FIG.1.



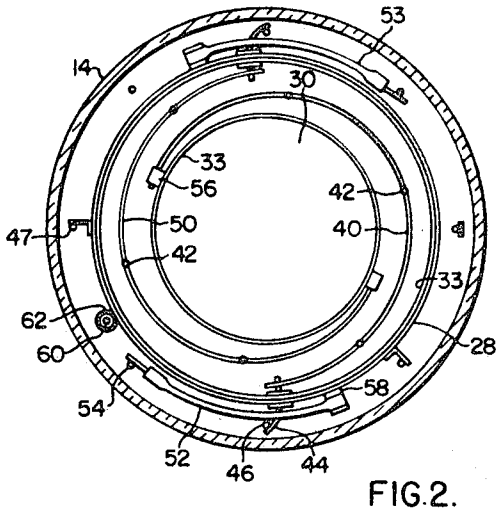
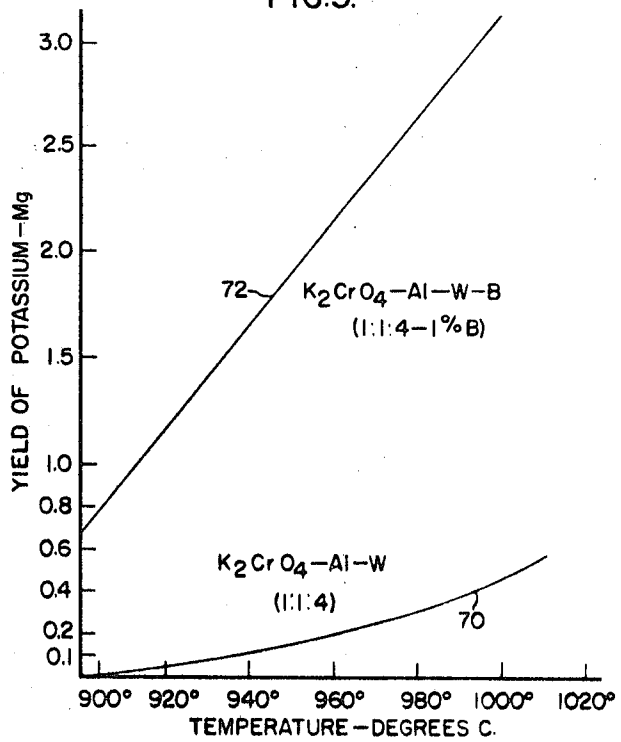




FIG.2.

FIG.3.




WITNESSES

Theodore F. Wrobel

James L. Young.

INVENTOR

Clayton D. Spangenberg

BY R. Lewis Dable

ATTORNEY

United States Patent Office 3,468,807 Patented Sept. 23, 1969



3,468,807

# ALKALI METAL GENERATOR

Clayton D. Spangenberg, Horseheads, N.Y., assignor to Westinghouse Electric Corporation, Pittsburgh, Pa., a corporation of Pennsylvania

Filed Nov. 19, 1965, Ser. No. 508,770
Int. Cl. C09k 3/00; C22b 27/00; H01j 39/22
U.S. Cl. 252—181.4 1 Claim

## ABSTRACT OF THE DISCLOSURE

An alkali generator including a portion of boron added to a mixture of an alkali chromate in combination with either aluminum and tungsten or silicon. The addition of an amount of boron in the approximate range between 0.1% and 10% by weight of the constituents of the generator will increase considerably the quantity of alkali metal produced.

This invention relates to photoemissive surfaces for electron image devices and more specifically to generator means for providing copious amounts of an alkali metal which reacts to form the photoemissive surfaces.

Photoemissive surfaces are typically employed in a variety of electron image devices such as television camera tubes, storage tubes, photomultipliers and others. Though the alkali generator of this invention could be utilized in various electron image devices, the invention will be described below with specific reference to a television camera tube of the image orthicon variety. Such a television camera tube typically includes an image section including a photoemissive surface formed on the end plate of the tube envelope and a thin glass target electrode spaced from the photoemissive surface. A light image is focused as by optical lenses onto the photoemissive surface which in turn generates a photoelectron image whose spatial distribution corresponds to that of the light image. The photoelectron image is accelerated and focused so as to strike the thin, glass target electrode with an energy sufficient to cause a secondary emission from the glass surface greater than unity. The secondary emission leaves a positive charge pattern upon the glass target surface corresponding to the light image focused upon the photoemissive layer. The opposite side of the glass target is scanned by an electron beam which approaches the target at a low velocity. Electrons from the scanning electron beam will be drawn to the positive areas of the target surface and will be deposited on the target to neutralize the positive potential pattern on this member. The beam of electrons discharges the surface of the target and the remainder of the electron beam is reflected back through the envelope of this device and is collected by an electron multiplier to form a video output signal of the television camera tube.

In the type of television camera tube described above, the photoemissive surface is formed upon an end plate of the envelope which is transmissive to the radiation which is to be sensed. Typically, a metallic material such as antimony is deposited upon the face plate as by evaporation. Next, an alkali such as cesium, potassium or sodium is generated and directed upon the layer of antimony. The alkali metal, as is well known in the art, reacts with the antimony layer to provide a photoemissive surface that has a spectral response over a range from the ultraviolet region to about 6400 angstroms. In the prior art, it has been found that the alkali generators are not as efficient as could be desired. Thus, in order to obtain sufficient quantities of the alkali metal, the generators have to be operated at temperatures close to that at which exothermic reactions and/or generation of large quantities of gas will occur. In the manufacture of such photoemissive surfaces, many devices may be lost due to the uncontrolled reaction that may occur when these alkali generators are operated at high temperatures. In many instances, this exothermic reaction or "burn-out" produces sufficient heat to destroy or substantially impair the operation of the electron image device being manufactured with the resultant waste of materials and labor.



It is thus an object of this invention to provide an improved photoemissive surface for electron image devices.

It is another object of this invention to provide an alkali generator capable of producing increased quantities of the alkali metal at lower, controlled temperatures.

It is a further object of this invention to provide a new and improved alkali generator whose operation may be more precisely controlled and whose use will result in improved photoemissive surfaces.

The invention, briefly, achieves the above mentioned and additional objects and advantages through the provision of an improved alkali generator including the combination of an alkali chromate as the basic source of the alkali metal and a portion of boron. In specific embodiments of this invention, boron is added to an alkali generator including portions of the alkali chromate, aluminum and tungsten and to an alkali generator including, portions of the alkali chromate and silicon. In accordance with the teachings of this invention, it has been found that the addition of an amount of boron in the approximate range of between 0.1% and 10% by weight of the constituents of the generator will increase the amount of alkali metal produced by as much as a factor of 10.

Further objects and advantages of this invention will be set out in the following description and in the drawings. For a better understanding of the invention, reference may be had to the accompanying drawings, in which:

FIGURE 1 is a partial, sectioned view of an electron image device such as an image orthicon including an alkali generator made in accordance with the teachings of this invention;

FIG. 2 is a sectional view of the image section of the image orthicon tube shown in FIG. 1 as taken along lines II—II of FIG. 1; and

FIG. 3 is a graph showing the production of an alkali metal of a generator without the addition of boron as compared with the novel alkali generator made in accordance with this invention.

Referring now to the drawings and in particular to FIG. 1, an electron image device **10** of the image orthicon variety is shown in which the alkali generator of this invention has been incorporated. In particular, the electron image device **10** includes a vacuum sealed envelope **12** comprising an enlarged portion **14** which contains the imaging section of this device, and an extended or neck portion **16** axially aligned with and sealed to the enlarged portion **14**. The neck portion **16** is sealed upon the end remote from the enlarged portion **14** with a base member **18** through which a plurality of terminals **20** extend for making electrical connections with external sources of potential. A writing electron gun (not shown) and the electron multiplier section (not shown) are normally incorporated within the neck portion **16**. At the other end of the envelope **12**, a face or end plate **22** encloses and seals the enlarged portion **14**.

Upon the interior surface of the face plate **22** there is deposited, as will be explained in greater detail later, a layer **24** of photoemissive material which will respond to a radiation image by generating an electron image whose spatial distribution corresponds to that of the radiation image. After the deposition of the layer **24**, a strip **34** of an electrically conductive material such as silver is applied over a portion of the layer **24** and extends along a portion of the inner periphery of the enlarged portion

14. A spring bias member 36 is secured as by spot welding to a stem terminal 38 and extends through a bottom segment of the enlarged portion 14. The spring bias lead 36 is so positioned by the terminal 38 to forcibly abut against the strip 34 and to make an effective electrical contact therewith. Also disposed within the enlarged portion 14 of the envelope 12 is the imaging section which includes a cylindrically shaped accelerating electrode 32 which acts to accelerate the electrons emitted by the photoemissive layer 24 onto a storage target 30 which is mounted within a cylindrically shaped electrode 28. More specifically, the target electrode 30 is mounted upon an annularly shaped support member 33 which has a U-shaped cross-section (see FIG. 1). The support member 33 is secured as by spot welding to the interior surface of the cylindrical electrode 28. Further, a cylindrically shaped electrode 26 is disposed remotely on the side of the electrode 28 from the photoemissive layer 24 for decelerating the electrons emitted by the writing electron gun (not shown) which is located within the neck portion 16. The electrodes 26, 28 and 32 are supported within the enlarged portion 14 as by a plurality of terminals which extend through the bottom segment of the enlarged portion 14 and which are secured to the various electrodes to make electrical connection therewith. Further, mechanical strength is added to this assembly by the inclusion of a plurality of support rods 60 (only one of which is shown for the sake of clarity) which are made of a suitable insulating material such as aluminum oxide and which are secured to the electrodes 26, 28, 32 as by a plurality of connecting tabs 62.

For a more complete description of the structure and the operation of such an image orthicon device, reference is made to U.S. Patent 2,682,479.

The mechanism for the deposition of the photoemissive layer 24 will now be explained in greater detail. As shown in FIGS. 1 and 2, small globules 42 of antimony may be attached to an evaporator filament 40 by melting the antimony and applying it to the filament 40 at temperature below evaporation. The melted antimony tends to wet the filament 40 and will cling to the filaments as globules 42 to be firmly attached upon cooling. Further, the evaporator filament 40 is supported within the support member 33 at one end as by a tab 56 which is secured to the member 33 and at the other end by a lead 44 which extends through and is supported by the cylindrical electrode 28. Further, it is noted that the filament 40 makes electrical connection as by the tab 56 to the cylindrical electrode 28 which is in turn electrically connected as by the stem terminal 47 to potential sources external of the envelope 12. The other end of the filament 40 is connected by the lead 44 which is electrically insulated with respect to the support member 33 and the electrode 28 by means well known in the art, and is electrically connected to a stem terminal 46. In this manner, the evaporator filament 42 is mounted within the envelope 12, close to the face plate 22, upon which the photoemissive layer 24 is to be formed. Two or more evaporator filaments may be arranged symmetrically about the axis of the face plate 22; illustratively, a second filament 50 is shown as in FIG. 2.

The source or generator of the alkali metal is provided by a plurality of channels made of a suitable electrically conductive material such as nickel and which contains the mixture of substances from which the alkali metal is to be generated. More specifically, the composition, which will be described in greater detail later, is inserted within a channel 52. The channel 52 is made from a strip of nickel metal and is rolled so as to form a hollow structure which is secured together as by spot welding. It is noted that the seam formed by the spot welding has a plurality of slits therein to allow the escape of the alkali metal. As shown in FIGS. 1 and 2, the channel 52 is mounted upon the cylindrical electrode 28 at one end by a tab 58 which is directly secured as by welding to the exterior periphery of the electrode 28. The other end of the channel 52 is secured as by spot welding to the stem terminal 54 which also serves to provide an electrical connection from a point external to the envelope 12. The substances within the channel may be heated by passing a current through the terminal 54, the channel 52, and the stem terminal 47.

The electron image device 10, in which the photoemissive layer 24 is to be formed, is first processed and evacuated, and then baked at a temperature in the approximate range of 375° to 400° C. for one hour to remove the occluded gases from the envelope 12. Then, as is well known in the art, the metal electrodes within the envelope 12 are then heated and degassed. After this normal processing of the device, an electric current is passed through the evaporator filament 40 by the use of the stem terminals 46 and 47 to heat the filament 42 to a temperature of approximately 525° to 550° C. which is sufficiently high for evaporating the antimony from the globule 42. In forming the photoemissive layer 24 on the surface of the face plate 22, the evaporator filament 40 is operated to deposit a sufficient amount of antimony to change the light transmission through the face plate 22 to approximately 90% of the normal light transmission through the plate 22 before any film is deposited. As is well known in the art, this can be easily determined by projecting a beam of light through the face plate 22 and measuring the intensity of this light beam upon a photocell connected to appropriate circuits. The antimony is allowed to evaporate onto the face plate 22 from the globule 42 until the desired thickness as is indicated upon the photocell has been reached.

As explained above, the source of the alkali metal is provided from the channels 52 and 53. In accordance with the teachings of this invention, a mixture of an alkali chromate is mixed with a portion of boron to provide an increased yield of the alkali metal. Typically, the mixture may be obtained by first pulverizing the materials and then mechanically mixing them in a vibrator. The mixed constituents are then pressed into pellets which are again pulverized as by a vibrating mixer. Finally, the materials are placed in the channels 52 and 53 as by hand. Though it has not been fully ascertained, a theory has been offered to explain the increased yield due to the addition of the small quantities of boron. It has been proposed that the boron acts as a scavenger to take away the oxygen from the chromate thereby more efficiently releasing the alkali metal. In a specific embodiment of this invention, the alkali chromate was mixed with portions of aluminum and tungsten. The alkali chromate is either potassium, sodium, cesium, lithium or rubidium chromate. In accordance with the teachings of this invention, it was discovered that an amount of boron in the range of about 0.1% to about 10% by weight of the total mixture was sufficient to achieve an increase of the alkali yield by a significant factor. If amounts of boron less than about 0.1% are added to the mixture, there is an insufficient amount of boron to react with the alkali chromate. On the other hand, if amounts of boron in excess of about 10% are added to the mixture, a violent exothermic reaction might occur when the mixture is heated. In particular examples, potassium chromate was mixed with additional amounts of either ¼% or 1% boron. In another illustrative example, potassium chromate was mixed with aluminum and tungsten in a ratio 1:1:2 with approximately 1% boron. Further, the alkali chromate was mixed with a reducing agent such as silicon and an amount of boron to obtain the desired increase of the alkali metal.

After the previously described step of applying a layer of antimony to the face plate 22, a sufficient electric current is passed through the stem terminals 54 and 47 to heat the channel 52 to a sufficiently high temperature of approximately 900° C. to cause a chemical reaction in the alkali chromate-boron mixture which will release

substantially pure alkali as a vapor in the enlarged portion **14** of the evacuated envelope **12**. During this evaporation of the alkali metal, the tube is maintained in the approximate range between 150° C. and 200° C. by being placed within an oven. This temperature maintains the alkali metal being generated within the tube in a vapor form and allows it to pass over and onto the layer of antimony and combine uniformly with the antimony layer. The alkali metal is continued to be deposited upon the face plate until the layer **24** provides a maximum photosensitivity. This may be determined by illuminating the photoemissive layer **24** with light during the evaporation of the alkali metal. An electric current through the stem terminal **38** to the photoemissive layer **24** is measured until it registers a maximum photoemission. When this occurs, the current through the channels **52** and **53** is stopped by turning off the applied voltage and the evolution of the alkali ceases. This method is sufficiently precise so that very little of the alkali metal beyond that necessary to properly sensitize the photoemissive surface is introduced into the tube.

In accordance with the teachings of this invention, it has been found that the addition of amounts of boron in the range of about 0.1% to 10% by weight of the total mixture of the alkali material has been found to result in increased quantities of the evolved metal. In particular tests, the results of which are shown in FIG. 3, the yield of the alkali metal was measured as a function of temperature for alkali producing mixtures with and without the addition of the prescribed amounts of boron. In the first instance, a mixture of potassium chromate, aluminum and tungsten was made in the ratios of 1:1:4 by weight and yielded when heated in amounts of alkali indicated by the curve **70**. In a second test, a 1% portion of boron was added to this mixture, i.e., potassium chromate, aluminum and tungsten in a ratio of 1:1:4, and the results of the yield of potassium are indicated by the curve **72**. As shown in FIG. 3, the yield of a mixture with a small portion of boron exceeded by a factor as much as 10 the same mixture without boron. In further tests with a mixture of potassium chromate and silicon, the addition of boron also produced an increase evolution of the potassium metal. Typical results for a mixture of potasium chromate and silicon in a ratio of 1:2 to 1:3 versus the same mixture with a 1% of boron yielded an average of 0.22 and 2.50 milligrams of alkali metal respectively.

Although the present invention has been described with a certain degree of particularly it should be understood that the present disclosure has been made only by way of example and that numerous changes and the details of construction and fabrication in the combination and arrangement of parts, elements and components can be resorted to without departing from the scope and the spirit of the present invention.

I claim:

**1.** A source for the generation of alkali metal comprising a mixture of potassium chromate, aluminum, tungsten and boron, the ratio of the weight of potassium chromate, aluminum and tungsten being about 1:1:4, said boron being present in said mixture in an amount in the range of about 0.1% to 10% by weight of said mixture.

**References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,236,647 | 4/1941 | McIlvaine | 252—181.4 |
| 3,096,211 | 7/1963 | Davis | 252—181.4 |

TOBIAS E. LEVOW, Primary Examiner

J. COOPER, Assistant Examiner

U.S. Cl. X.R.

75—66; 252—188.3; 313—65