Jan. 12, 1960 T. A. CHUBB 2,921,216

COPPER-AMINE-COMPLEX GAS PHOTOCELL

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FIG. 1

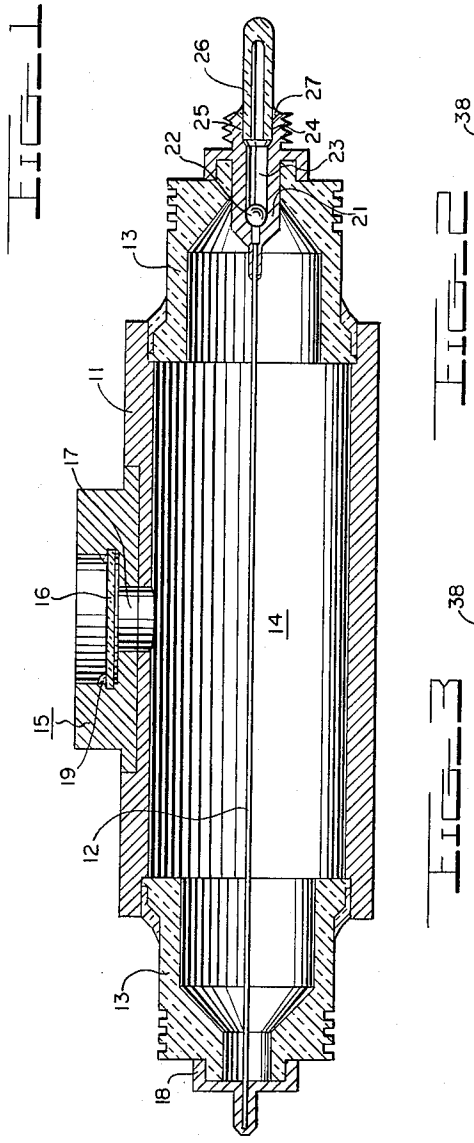


FIG. 2

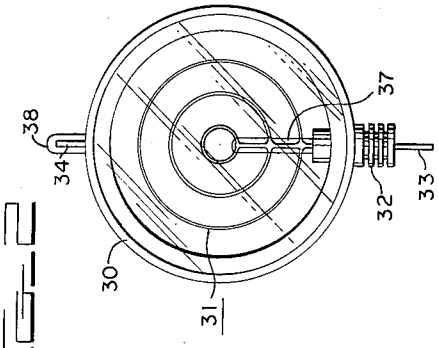
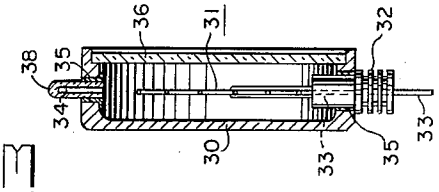


FIG. 3



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COPPER-AMINE-COMPLEX GAS PHOTOCELL

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9 Claims. (Cl. 313—100)

(Granted under Title 35, U.S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

The invention relates to a gas photocell and in particular to a gas photocell which is designed to operate effectively in the spectral region between 2200 and 4400 Angstroms.

The invention is directed to a gas photocell which may be (1) of the type that does not make use of gas ionization or (2) of the type in which gas gain occurs through avalanche ionization of the contained gas. Whether a gas photocell is affected by gas amplification or not, the enclosed gas can produce an effect on the spectral characteristics. However, in the prior art the practice has been to employ inert gases which are stable and do not react with the cathode surfaces. Any reaction involving the gaseous component has as a rule produced undesirable effects in the performance of these tubes. Photocells have been developed which operate in the ultraviolet and visible regions but these tubes contain alkali metals—materials which are difficult to maintain in pure form. These tubes are generally not recommended for use at gas gains higher than about 20.

The gas photocell of the present invention encloses a reactive gas or vapor which interacts chemically with the metal cathode, and as a result of such reaction, the cathode becomes sensitized to the spectral region of near ultraviolet and in the blue range of visible light. The novel cathode retains this sensitivity as long as it remains in contact with the reactive gas. The chemically active gas reacts with the metal initially to form a metal complex as the sensitized surface on the cathode, said metal complex is sufficiently stable in the presence of chemically active gas in the photocell to provide a gas photocell which increases its sensitivity in the direction of longer wavelengths. The new gas photocell does not lose its sensitivity with respect to time or with prolonged operation.

More specifically, the reactive gas or vapor is an organic amine, such as methylamine gas, that reacts with or complexes with the cathode metal, preferably copper, to form a copper-amine-complex surface on the cathode. Methylamine gas molecules form the gaseous filling in the photocell. The methylamine gas remains in equilibrium with the copper-amine-complex surface whereby during the operation of the photocell the methylamine gas is undergoing a slow reaction with the copper cathode, and the copper-amine-complex may be dissociating slowly to release amine molecules.

It is accordingly, an object of the present invention to provide a stable gas photocell sensitive in the region between 2200 to 4400 Angstroms which is capable of operating at a gas gain of up to 10,000.

Another object of the present invention is to provide a photocell which is extremely stable with respect to time and without any noticeable change in its electrical characteristics.

A further object of the present invention resides in the provision of a photocell with a novel sensitized cathode in which the sensitized cathode remains sensitive as long as it is in contact with the gaseous filling.

Other objects of the present invention will become apparent from the following detailed description when considered with the drawings in which:

Fig. 1 is a longitudinal section of a photocell with gas amplification which incorporates the novel features of the present invention;

Fig. 2 is a cross-sectional view of a photocell without gas amplification, which utilizes the sensitized cathode in accordance with the teachings of this invention; and

Fig. 3 is a frontal view of the photocell shown in Fig. 2.

Referring now to the drawings, there is shown in Fig. 1 a gas photocell having an electron-emitting metal envelope **11** made preferably of copper, but other metals, for instance, silver, may also be utilized for this purpose. The metal envelope is coaxially arranged with respect to an anode wire **12** which is composed of substantially pure tungsten; the wire is centrally located within the metal envelope and insulated therefrom at each end by any suitable means, such as, ceramic end portions **13** which also confine the envelope space **14**. The ceramic end portions are sealed to the metal envelope with an epoxy cement or any other suitable means. The photocell is provided with a light-transmitting window **15** having a 96%-silica type glass **16** that transmits light through opening **17** onto the interior surface of the metal envelope. The glass **16** is sealed to the metal with an epoxy cement, shown at **19**.

The anode wire is soldered to a metal ring **18** at one end of the cylindrical photocell, while the other end of the wire is supported by wire support terminal **21** by passing a metal bead **22**, which is soldered to the anode wire, through a slitted opening **23**. The wire support terminal **21** extends through the ceramic end portion **13** and emerges on the other side as a threaded lug **24** on which a protective cap (not shown) may be attached for the safety of glass seal **26**. A glass outlet tube **25** communicates with the tube space **14** through the slitted opening **23** through which the tube may be evacuated and filled with gas or vapor in accordance with the teachings of this invention. After the tube has been evacuated and filled with the desired filling, glass seal **26** is formed to retain the gaseous content within the tube.

The copper cathode gas photocell made in accordance with this invention is initially cleaned to provide a surface free from dirt; it is then evacuated and an organic amine is introduced therein by any convenient means. A typical amine that may be used is methylamine gas, although other organic amines such as ethylamine, propylamine, ethylenediamine, etc., may also be used. In the preferred embodiment of a gas photocell with gas amplification as shown in Fig. 1, 30 millimeters of methylamine are introduced into the photocell and a sufficient time is allowed for a portion of the amine to react or complex with the copper metal to form a copper-amine-complex, which imparts a bluish tint to the copper surface. The amine is introduced in sufficient quantity so that after the copper-amine-complex has formed, a portion of the amine remains in the photocell space to provide for the gas ionization which is required in the operation of this type of photocell.

A photocell of the type which is not affected by gas amplification may also incorporate the teachings of the present invention. A photocell as shown in Figs. 2 and 3 has an amine vapor present in the envelope space and a sensitized cathode surface consisting of a metal-amine-complex. The operating voltage is considerably less than that for the photocell of Fig. 1. In Fig. 2 the photocell has an envelope **30** constructed of a metal such as copper or silver, which serves as the cathode and a window with a glass **36** of a high silica composition such that it will transmit radiation in the near ultraviolet and visible regions of from about 2200 A. to about 4400 A. The

anode is formed by concentric chrome iron loops 31 that are soldered to the anode terminal wire 33, and the anode assembly is centered in the envelope relative to the window and rear cathode surface and insulated from the metal envelope by a ceramic insulator 32. The anode assembly is provided with an insulating material 37 which covers the soldered connections along the anode terminal wire 33. The outlet gas tube 34 provides a means for evacuating and filling the photocell while glass seal 38 retains the gaseous filling in the tube. The outlet gas tube and ceramic insulator are secured to the metal envelope with an epoxy cement 35 or by any other means.

After the tube has been cleaned to remove any dirt, the photocell receives 15 millimeters of methylamine gas and a sufficient period is allowed for the reaction to take place. When the methylamine gas has reacted or complexed with the copper surface a bluish tint appears throughout the interior surface of the copper envelope. A portion of the amine remains in the tube space to provide a reservoir of said gas which remains in equilibrium with the copper-amine-complex surface. This gaseous amine maintains the copper-amine-complex by reforming or complexing anew any of the copper-amine-complex that dissociates in the operation of the tube.

Whenever light in the spectral region between 2200 and 4400 Angstroms impinges on the sensitized surface, photoelectrons are drawn out of the cathode metal. If a sufficiently high voltage is applied across the tube, the released electrons will ionize the amine gas molecules and a series of gas ionization amplify the initial photoelectric current from the cathode. In the gas photocell shown in Fig. 1, where the operating voltage is in the neighborhood of 1400 volts, the gas ionizations fan out rapidly, each electron displaces additional electrons as it drifts swiftly toward the anode. The result is a gas amplification of nearly 10,000. In the photocell shown in Figs. 2 and 3 which operates with a voltage of about 90 volts, the displaced electrons do not gain energies sufficient to cause ionizations and the output is nearly equal to the emitted photoelectron current.

The novel treatment of the copper cathode as described herein results in a sensitized cathode surface which shifts the sensitivity of the photocell from the spectral region common to copper to a region of longer wavelengths. This shift in sensitivity is more than 1000 Angstroms in the direction of visible light. Pure copper metal is not so sensitive to wavelengths in the near ultraviolet and visible light, in fact, such sensitivity is usually obtained from alkali metal coatings on metal cathodes. The copper-amine-complex sensitizes the copper cathode so that the photocell is now unusually sensitive to near ultraviolet radiation between 3000 and 4000 Angstroms.

A photocell constructed in accordance with the teachings of this invention has an operable range from about 2200 to about 4400 Angstroms. As a result of this invention it is possible to employ a copper cathode which normally has negligible photosensitivity in the visible portion of the spectrum and to convert it to a surface which has a high photosensitivity to visible light.

As a result of the sensitized copper-amine-complex cathode surface and the methylamine gas in the photocell space, the tube is stabilized considerably, that is, it is capable of a long operable life without loss of its efficiency and without change in the electrical characteristics of the tube. It may be inferred theoretically, that an equilibrium is established between the cathode surface and the enclosed amine: The amine gas replenishes any amine that is decomposed or released from the metal-amine-complex during the operation of the tube. The dissociation product from the cathode is usually an amine molecule, so the photocell does not suffer from contaminations which often limit the lifetime of gas-filled tubes.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A gas photocell comprising a metal envelope which serves as the cathode, a centrally arranged anode, a window in said envelope that transmits ultraviolet and visible light and a gaseous filling which consists of an organic amine wherein a portion of said amine reacts with the metal cathode to form a metal-amine-complex on said cathode.

2. A gas photocell as claimed in claim 1 in which the amine is methylamine.

3. A gas photocell as claimed in claim 1 in which the amine is ethylenediamine.

4. A gas photocell comprising a copper envelope which serves as the cathode, a coaxial anode, a window in said envelope that transmits ultraviolet and visible light and a gaseous filling consisting of methylamine wherein a portion of said methylamine reacts with the copper cathode to form a copper-amine-complex on the cathode.

5. A gas photocell comprising a copper envelope which serves as the cathode, a coaxial anode, a window for transmitting radiation in the ultraviolet and visible light and a gaseous filling consisting of an organic amine wherein a portion of said amine reacts with the copper cathode to form a copper-amine-complex on the cathode while the remaining amine replenishes any of the amine that is decomposed from the copper-amine-complex on said cathode.

6. A gas photocell comprising a copper envelope which serves as the cathode, a coaxial anode, a window which transmits radiation in the range of about 2200 to about 4400 Angstroms and a gaseous filling consisting of an amine wherein a portion of said amine reacts with the copper cathode to form a copper-amine-complex while the remaining portion of amine replenishes any of the amine that is decomposed from the copper-amine-complex on said cathode.

7. A gas photocell comprising a copper envelope which serves as the cathode, a window in said envelope that transmits ultraviolet and visible light, an anode centrally disposed with respect to said envelope and said window and a gaseous filling consisting of methylamine wherein a portion of said methylamine reacts with the copper cathode to form a copper-amine-complex on the cathode.

8. A gas photocell comprising a copper envelope which serves as the cathode, a window in said envelope that transmits ultraviolet and visible light, an anode centrally disposed with respect to said envelope and said window and a gaseous filling consisting of an organic amine wherein a portion of said amine reacts with the copper cathode to form a copper-amine-complex on the cathode while the remaining amine replenishes any of the amine that is decomposed from the copper-amine-complex on said cathode.

9. A gas photocell comprising a copper envelope which serves as the cathode, a window in said envelope that transmits radiation in the range of about 2200 to about 4400 Angstroms, an anode centrally disposed with respect to said envelope and said window and a gaseous filling consisting of an amine wherein a portion of said amine reacts with the copper cathode to form a copper-amine-complex while the remaining portion of amine replenishes any of the amine that is decomposed from the copper-amine-complex on said cathode.

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