

April 28, 1959

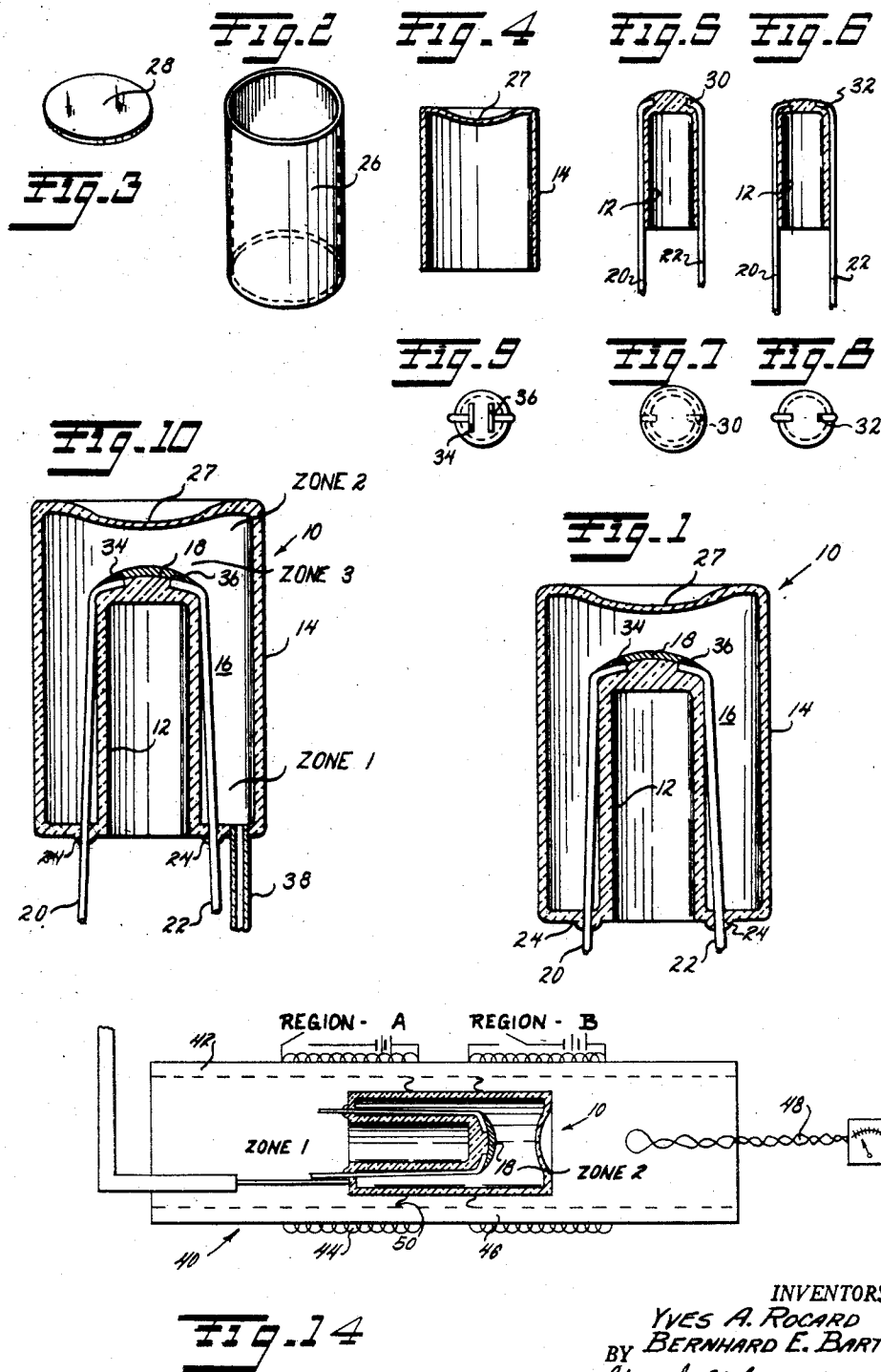
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2,884,345

INFRA-RED DEVICES AND METHODS

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3 Sheets-Sheet 1



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Fig. 11

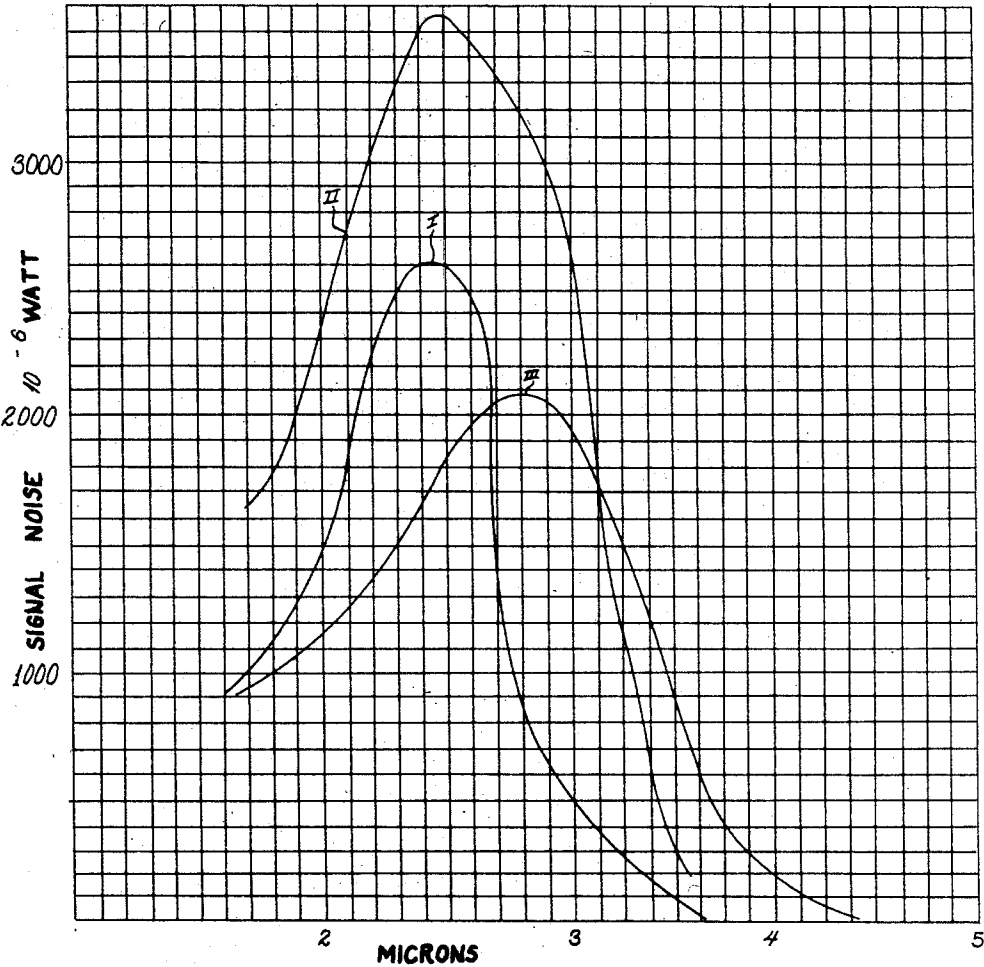
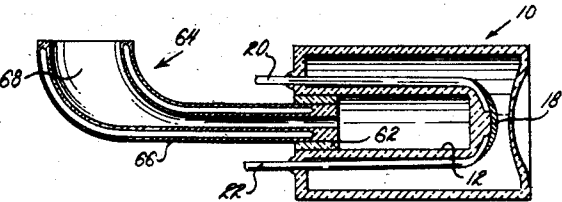


Fig. 12

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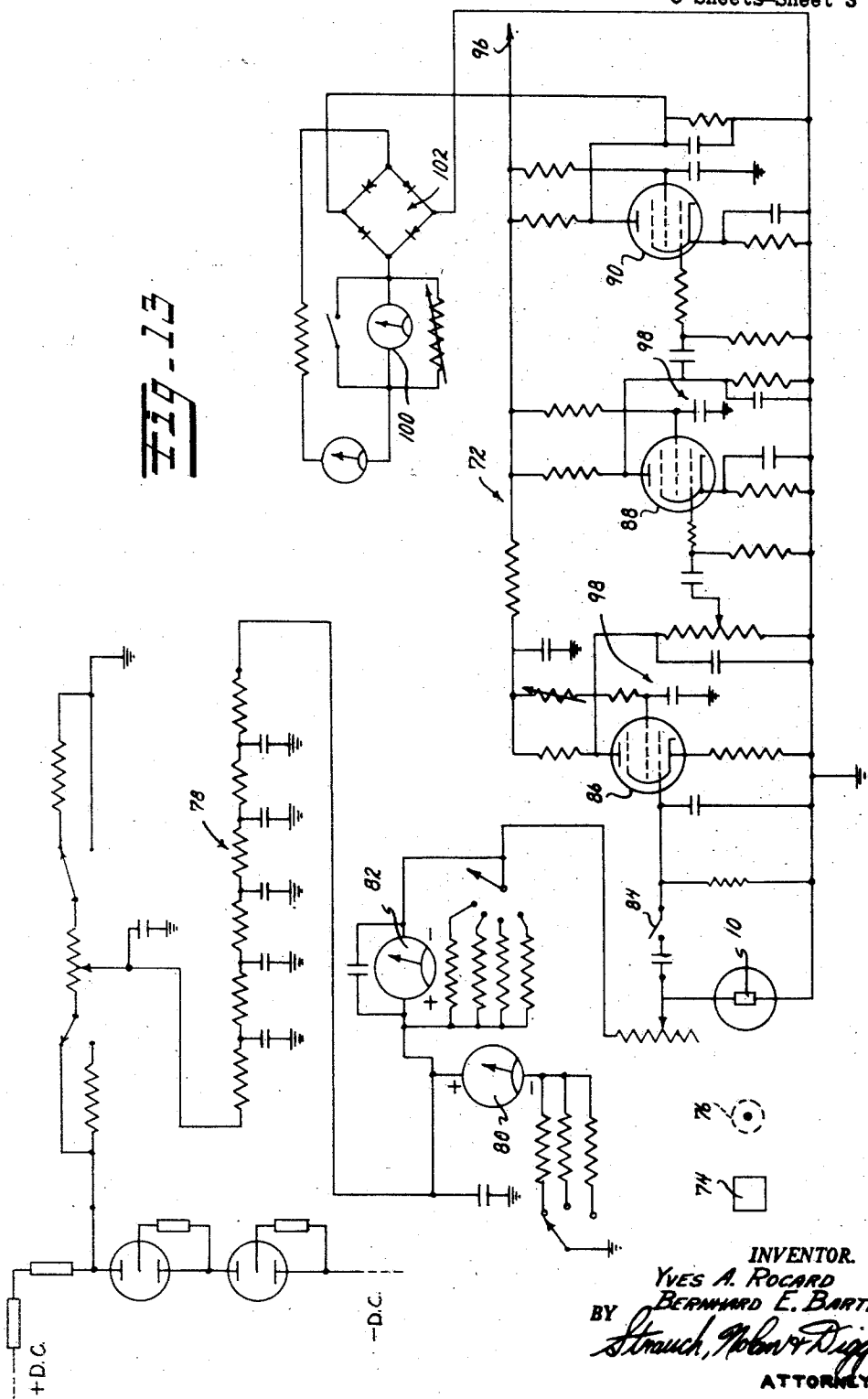
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INFRA-RED DEVICES AND METHODS

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4 Claims. (Cl. 117—201)

This invention relates to improvements in the production of infrared responsive cells, and particularly in such cells of the evaporated layer type.

Infrared responsive cells of the evaporated layer type have heretofore been produced as disclosed, for example, in U.S. patent to Cashman No. 2,448,516, and as described in vol. 115 at page 1 of the January 1952 issue of Science in an article entitled "Photoconductive Cells for Detection of Infrared Radiation," and vol. 159 at page 818 of the June 14, 1947, issue of Nature in an article entitled "Lead Sulfide Photoconductive Cells." Such cells are, however, relatively unstable, with low sensitivity and low signal-to-noise ratio. The prior methods of producing such cells are not adapted to producing cells having predetermined reproducible characteristics and this results in high production costs due to the high percentage of unsatisfactory cells.

It is, accordingly, an object of this invention to provide a new and improved method of producing photocells of improved response to infrared radiations, together with improved stability, high sensitivity, high signal-to-noise ratio coupled with a low time constant.

Another object of the present invention is the provision of an improved method of producing such cells having predetermined predictable characteristics and hence providing for relatively low cost mass production.

It is also an object of this invention to provide a photocell having a new and improved structure.

A further object of this invention is to provide a photocell of novel cooling means.

Other objects will become apparent in the disclosure herewith in conjunction with the accompanying drawings and the appended claims and in which:

Figure 1 is a sectional view of a complete photocell; Figures 2 to 9 are views of the components of the cell of Figure 1 to illustrate steps in the assembling of the components;

Figure 10 is a sectional view of the photocell at one step in its manufacture;

Figure 11 is showing by way of example, of response curves of a specific lead sulfide photocell under particular temperature conditions;

Figure 12 is a sectional view of an assembly for cooling a photocell;

Figure 13 is a wiring diagram of one form of testing amplifier and of other test equipment; and

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Figure 14 is a plan view of an electric oven, and shows heating zones and a photosensitive cell in the heating zones.

Figure 1 shows a complete infrared responsive cell 10, which comprises a body of a suitable glass which defines an inner thimble 12, and an outer envelope 14, integrally connected with the thimble to define a chamber 16. A layer 18, of a radiation sensitive lead sulfide sits on top of the thimble, and wires 20 and 22, respectively, are connected to the sensitive layer and extend through the envelope at suitable seals 24. The wires 20 and 22 are of tungsten or of other suitable materials capable of being fused with the glass. The upper end of the body is depressed, as indicated at 27, to form a relatively thin window portion of the body. The body is formed in steps of taking a glass tube 26 (Figure 2) of an external diameter of about 30 mm., and of a wall thickness of 1 mm., and a glass plate 28 (Figure 3) about 0.5 mm. thick and of a diameter of about 25 mm. and fusing them together to make the outer protective envelope 14. An indentation is made in the plate 28 to stretch the glass and make the thin window 27.

The inner glass unit or thimble 12, is formed of a glass tube (Figure 5) having an outside diameter of about 18 mm. and 1 mm. thick, and the upper end of the tube is sealed with a flame, and during this operation the two wires 20 and 22, are embedded in the glass, as indicated at 30 (Figures 5 and 7). The glass is next ground to expose the upper ends of the wires, as indicated at 32 in Figures 6 and 8. The wires are then ground with a very fine abrasive and polished until the ends are perfectly flat and free from scratches. This is a very important operation because any roughness at these points will cause noise and so decrease the signal to noise ratio in the cell.

Electrodes are next applied to the exposed tungsten contact points to define lines 34 and 36, respectively (Figure 9) and it is essential that these lines be parallel and of even width. The effective area of the sensitive material is measured between these two lines. The optimum area is 11 x 4 mm. although any other area can be employed, and cells with sensitive areas of 5 x 5, 4 x 4 and 3 x 3 mm. have been produced and have operated satisfactorily. Of course, with smaller cell areas the amount of total energy impinging on the sensitive area is less and the optimum characteristics may decrease.

The tungsten wires are connected to the sensitive layer through the electrodes 34 and 36. The electrodes are preferably formed of a deposit of Aquadag which is a colloidal graphite-suspension in an aqueous or non-aqueous vehicle.

As shown in Figure 10, the thimble and the outer protective envelope are assembled and sealed together, and a capillary tube 38 communicates with the chamber 16. This tube has an external diameter of 6 mm. and an internal diameter of 1 mm. This tube provides for the introduction of the powder used in the production of the sensitive layer 18, for the introduction of oxygen, and for the exhausting of gas from the chamber, and is re-

moved, and its entry point sealed off when formation of the cell has been completed.

Moisture, even in the smallest amounts, will cause unpredictable operation of the cell and every precaution must be taken to make certain that the materials placed in the cell are perfectly dry.

Preferred methods for the preparation of the lead sulfide powder for the cell are now described. For example, in a wet method of lead sulfide preparation, purified hydrogen sulfide is passed into a 1 molar solution of lead nitrate or lead acetate or the like. The pH of this solution will be approximately 5.55 for the lead acetate and 3.10 for the lead nitrate. Preferably the amount of hydrogen sulfide used is calculated so that no more than about one-third of the lead salt present in the solution will combine with the hydrogen sulfide to form a precipitation of lead sulfide. The undesirable impurities are precipitated in this first step. The solution is filtered and this first precipitation is discarded. The concentration of lead salts of this solution will then be about two-thirds molar and will have a pH of about 5.59 for lead acetate and 3.32 for lead nitrate. Hydrogen sulfide is again introduced in the manner and quantity described above and the lead sulfide produced from the second precipitation is filtered and dried. The second precipitation contains the least impurities and is acceptable for use in the production of infrared sensitive layers. The remaining solution will have a lead salt concentration of one-third molar and a pH of approximately 5.70 for the lead acetate and 3.70 for the lead nitrate. This remaining solution is discarded because the remaining unprecipitated lead salts contain undesirable impurities which interfere with the photosensitivity of the final product.

A dry method for preparing the lead sulfide has the advantage of yielding a moisture free product, and in this method purified metallic lead is evaporated into an atmosphere of hydrogen sulfide. A vacuum furnace or muffle furnace can be used. The lead sulfide powder is collected and placed in a desiccator until required. Another method of preparing dry lead sulfide powder is to react purified lead metal with purified sulfur in stoichiometric proportions in a vacuum. The resultant product is collected and stored in a desiccator.

A preferred method of producing the lead sulfide sensitive area within the cell is as follows:

About 5-7 milligrams (depending on the cell size) of the lead sulfide powder, which has been prepared in the manner described above, is passed into the chamber 16 of the cell body, through the tube 38, and is initially in zone 1, indicated in Figure 10. The chamber 16 is now evacuated down to pressure of 10^{-5} or 10^{-6} mm. of mercury. The lead sulfide is next transferred from zone 1 to zone 2, indicated on Figure 10 by sublimation. To effect this transfer, the cell is placed in a small oven as shown in Figure 14. The temperature of the oven in the region A should have a minimum value of 580 degrees centigrade, while the temperature in region B should not exceed 550 degrees centigrade.

The lead sulfide now at zone 2 is oxidized by introducing oxygen while the temperatures in region B are still about 580° C. The amount of oxygen used is such that from 1-50% of the lead sulfide deposited on the area between the electrodes is oxidized. Approximately 30% oxidation of the lead sulfide layer is preferable. The amount of oxygen used is determined by calculating the oxygen required to oxidize approximately 30% of the lead sulfide in the cell envelope and proceeding as follows:

The volume of the vacuum device used in the cell manufacturing procedure is determined and a measured amount of oxygen is introduced into the system. The resulting pressure of the oxygen in the vacuum device is recorded. The reaction between the oxygen and the

lead sulfide in the cell will cause a change in the pressure of the oxygen in the vacuum unit. The oxidation procedure is allowed to proceed until the change of pressure in the system indicates that a sufficient amount of oxygen has reacted with the lead sulfide, so that approximately 30% of the lead sulfide has been oxidized and optimum sensitivity results.

The oven 40, of Figure 14, may be of the form of a tube 42, upon which is placed a first heating coil 44 of suitable wire to produce the temperature desired in region A, and a second heating coil 46, is disposed about the tube to produce the temperature desired in region B, and suitable independent thermocouple means, such as is indicated at 48, are inserted in the oven from each end so that the operator may observe the temperature in each region. Conventional means may be employed to automatically control current flow to the heaters to maintain the temperatures at the desired values.

The oven may be provided with suitable means 50 to position the cell radially within the oven.

When the control tests which will be described in detail hereinafter, indicate that the oxidation procedure should be terminated, the cell is again evacuated down to 10^{-5} or 10^{-6} mm. and the cell envelope is heated so that all of the sublimated lead sulfide remaining around the inside of the envelope is transferred to zone 2. The desired portion of the envelope may be heated by a hand-held gas burner or by the proper disposition of the cell in the oven. The next step is to heat the envelope so that the lead sulfide is transferred by sublimation from zone 2 to zone 3, indicated in Figure 10. During this transfer of the material, the temperature of zone 3 should be higher than 100° C. to prevent simultaneous condensation of sulfur vapor. A temperature of 150° C. has been found satisfactory especially for photocells to be sensitive at room temperature. At the completion of this transfer, the effective lead sulfide will be on the area defined between the electrodes 34 and 36 and in conductive connection with those electrodes. Oxygen is again introduced into the cell at a pressure of 0.2 mm. The cell is again placed in the oven, and its temperature is raised until the temperature in zone 2 is 500 degrees centigrade, and the temperature at zone 3, should be no more than 400 degrees centigrade. The cell is maintained at these temperatures, and with the difference of temperature given above, for from about one half to five minutes, depending on the size and shape of the cell. The cell is then cooled rapidly to room temperature by interrupting the current to the heating coils and by directing a blast of cold air internally of thimble 12, and against the upper end of the thimble to cool the layer of radiation sensitive material now in zone 3.

An important distinguishing feature of the improved method of the present invention resides in the separation of the sublimation and oxidation operations into distinct steps permitting much greater control over activation of the sublimed lead sulfide and resulting in cells of substantially identical characteristics.

After the cell has been cooled, it is then evacuated down to 10^{-5} or 10^{-6} mm. and its resistivity is measured. The dark current for one volt applied to the cell may be approximately 10 microamperes as a maximum. The photocurrent is then measured when the cell is irradiated for example by a black body radiator operating at a temperature of 300 degrees centigrade, and having an emitting orifice of one centimeter square, and placed at a distance of approximately 27 mm. from the cell. The photocurrent should then, in this example, be more than three microamperes.

If the results of this testing procedure indicate that the cell is satisfactory, the cell is completed by flame sealing the capillary tube 38, close to the base of the cell. If the tests indicate that the cell has not met the standards for light and dark currents, the cell is evacuated to

10⁻⁵-10⁻⁸ mm. and heated at 200° C. for 1-2 minutes, immediately cooled and retested. This procedure can be repeated again if the dark currents still are not satisfactory. The above procedure increases the resistance of the cell, so that optimum characteristics will result.

Moisture must be excluded at all steps for, while moisture may make the photo-sensitive material more sensitive under certain conditions, it makes the operation of the cell unpredictable.

In Figure 11 there is shown the spectral sensitivity curves of the lead sulfide cell prepared in the manner described hereinbefore. The cell was irradiated by a black body having an emitting orifice of one centimeter square and placed at a distance of 80 cms. from the cell, and the input to the cell was modulated at 400 cycles per second so that the output of the cell could be measured at the output of an amplifier having a band pass within the range of 50 to 5000 cycles per second, and so that the noise range of the cell could be measured.

The solid line I gives the output response of a given lead sulfide cell held at a temperature of 20 degrees centigrade; the solid line II gives the response of the cell when held at a temperature of minus 80 degrees centigrade; and the solid line III gives the response of the cell when held at a temperature of minus 180 degrees centigrade. The curves also show how the peak of the response is related to the irradiation in terms of wave length in microns.

The time-constant of the lead sulfide cell made in the manner hereinbefore described is of the order of 10⁻⁴ seconds when the cell is at a room temperature of 20 degrees centigrade. The signal to noise ratio ranges from about 300 to 1 for a grade C cell to as high as 500 to 1 for a grade A cell.

The working spectral sensitivity of the cell is to wave lengths of about 3 microns at room temperature and to about wave lengths of 4.5 microns at minus 180 degrees centigrade.

In Figure 12 there is shown one means for holding the lead sulfide cell at a low temperature. The lead sulfide cell 10 has a portion of the wall of the thimble 12, treated to present a ground surface, as indicated at 62. A body 64, is of a double-wall construction, as in the familiar Dewar flask in which there is a vacuum in the space between the two walls, and a shank portion 66, of the body has a ground glass and portion and is entered in the thimble 12, to make a tight fit with the surrounding ground glass portion of the thimble. The body 64, also has a bowl portion 68, communicating with the shank, and when liquid air is poured into the bowl it flows into the interior of the thimble to hold the radiation sensitive material 18 at the desired low temperature.

When the body 64 and the communicating interior of the thimble are filled with about 200 cubic centimeters of liquid air the cell will operate at a temperature of about minus 180 degrees centigrade for an hour without recharging of the device with liquid air.

Figure 13 shows diagrammatically an amplifier 72, connected to a cell such as has been described hereinbefore to amplify the output of the cell with a gain of the order of one million and a band pass of from 50 to 5000 cycles per second. In addition to the amplifier, the diagram of Figure 13 shows means for indicating the photo-cell current and the output current of the amplifier, etc., such as are used in checking the condition of the cell as it is being made, and mentioned hereinbefore as the control checking of the cell before it is finally sealed and as having met the desired requirements for the cell.

During the sensitizing of the lead sulfide layer of the cell, and when the cell has been completed, the factory testing procedure includes the use of a black body 74, at a temperature of 300 degrees centigrade and with an

emitting orifice of one centimeter square and placed at a distance of 80 cms. from the cell. This irradiates the cell 10, through a radiant energy beam chopping device 76 which passes pulses of energy at a frequency of 400 cycles per second to the cell. The low chopping frequency is used so that the cell is tested under its poorest service operating condition rather than at its optimum frequency of 800 cycles per second at which the ratio of signal to noise is markedly higher. The polarizing voltage is 100 volts.

Voltage is applied to the cell from a suitable source of D.C. voltage through voltage regulator means and through a filtering network 78. The applied voltage is indicated by a meter 80 and the photocell current, by a meter 82 while the cell is disconnected from the amplifier by a switch 84 in the first control tests and the chopper is not being used.

In the subsequent test, the switch 84 is closed and the chopper 76 is operating. The output of the cell is fed to the control grid of the first pentode tube 86; the amplified output from this tube is fed to the control grid of a second pentode tube 88; and its output is fed to the control grid of a third pentode tube 90. The anode circuits of the tubes are fed from a suitable source of D.C. voltage through a terminal 96. Bandpass filters are provided in the stages of the amplifier by capacitance-resistance networks 98 and the stages are resistance-capacitance coupled. A current indicating instrument 100, may be connected in the output circuit of the amplifier through a bridge network 102 of rectifiers, so that a sensitive D.C. meter can be utilized to indicate the pulsating output.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

What is claimed and desired to be secured by United States Letters Patent is:

1. In the method of producing a photocell in an envelope which contains an interior upstanding thimble therein and with the thimble having electrodes thereon, the steps which comprise placing dry lead sulfide powder in the envelope, then subliming said powder, then condensing the vapor on a surface above the thimble partially oxidizing the condensed vapor, then subliming the lead sulfide again and condensing the vapor to deposit a layer of the sulfide on the electrodes before completing the oxidizing process.

2. In the method of producing a photosensitive lead sulfide cell, the method which comprises providing a cold envelope in which lead sulfide is collected on a wall, then heating the envelope in the region of the collected lead sulfide to one temperature while heating the envelope in the region of a pair of electrodes to a lower temperature so that the lead sulfide is transferred from the wall to the electrodes, introducing oxygen into the envelope after the lead sulfide is transferred to the electrodes and maintaining the presence of oxygen in the envelope for a period of time while the elevated temperature of the regions is maintained, and finally cooling the envelope rapidly to room temperature.

3. In the method defined in claim 2, the additional step of cooling the cell rapidly by directing a blast of cooling medium onto the outer surface of said cell to be effective at the region containing the lead sulfide material.

4. In the method of producing a photosensitive cell, the method which comprises the steps of entering a quantity of lead sulfide into a first zone in an envelope, then evacuating gas from said envelope, then transferring the

lead sulfide from said first zone to a second zone at a second position in said envelope by sublimation by maintaining the temperature of the envelope in the region of the first zone at a higher temperature than the temperature of the envelope in the region of the second zone, introducing oxygen into the envelope while the sublimed material is in the second zone while maintaining an elevated temperature in the region of the envelope about the second zone substantially constant for a period of time necessary to cause partial oxidation of the lead sulfide in said second zone, then evacuating said envelope, heating the envelope in the region of said second zone to cause evaporation of the lead sulfide onto a third zone including spaced electrodes, then introducing oxygen into the envelope while maintaining the third zone at an elevated temperature to complete the activation of the lead sulfide, and then rapidly cooling the envelope to room temperature.

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