

Oct. 28, 1958

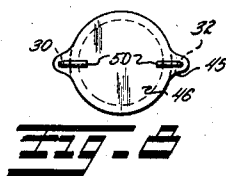
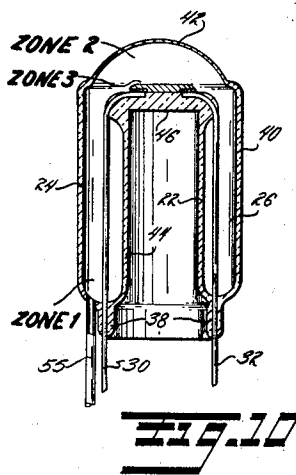
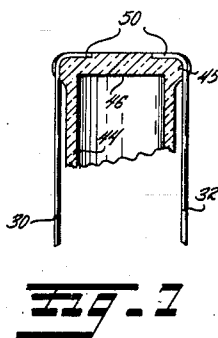
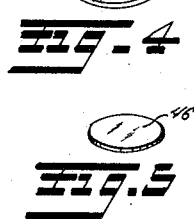
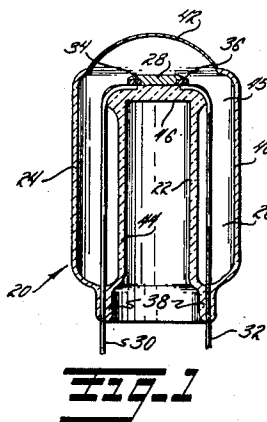
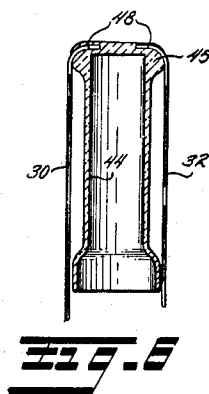
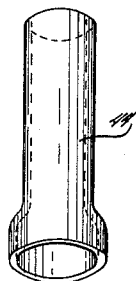
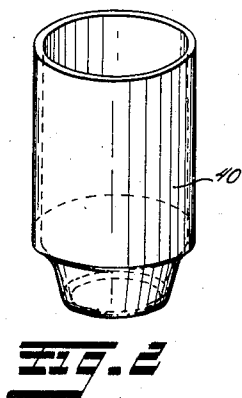
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2,858,398

INFRA-RED SENSITIVE PHOTOCELLS

Filed June 8, 1954

4 Sheets-Sheet 1



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4 Sheets-Sheet 2

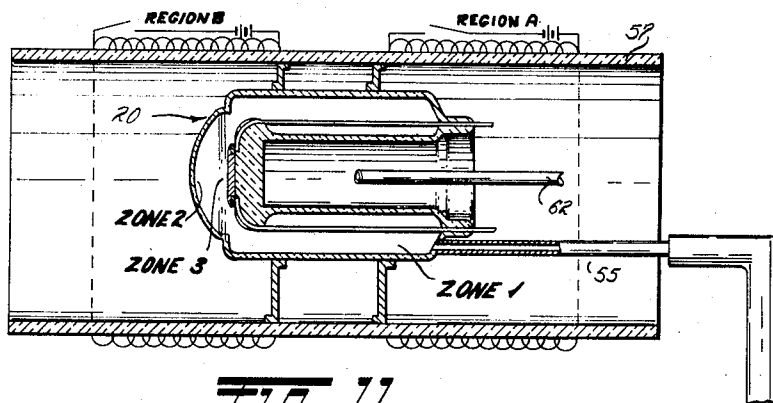


Fig. 11

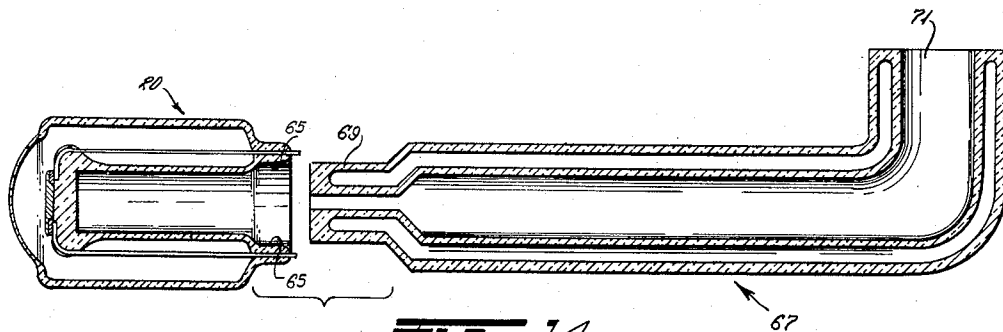


Fig. 14

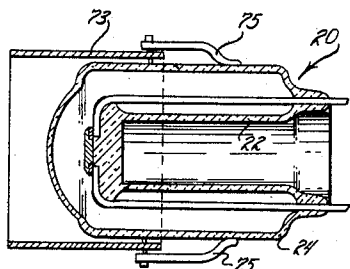


Fig. 15

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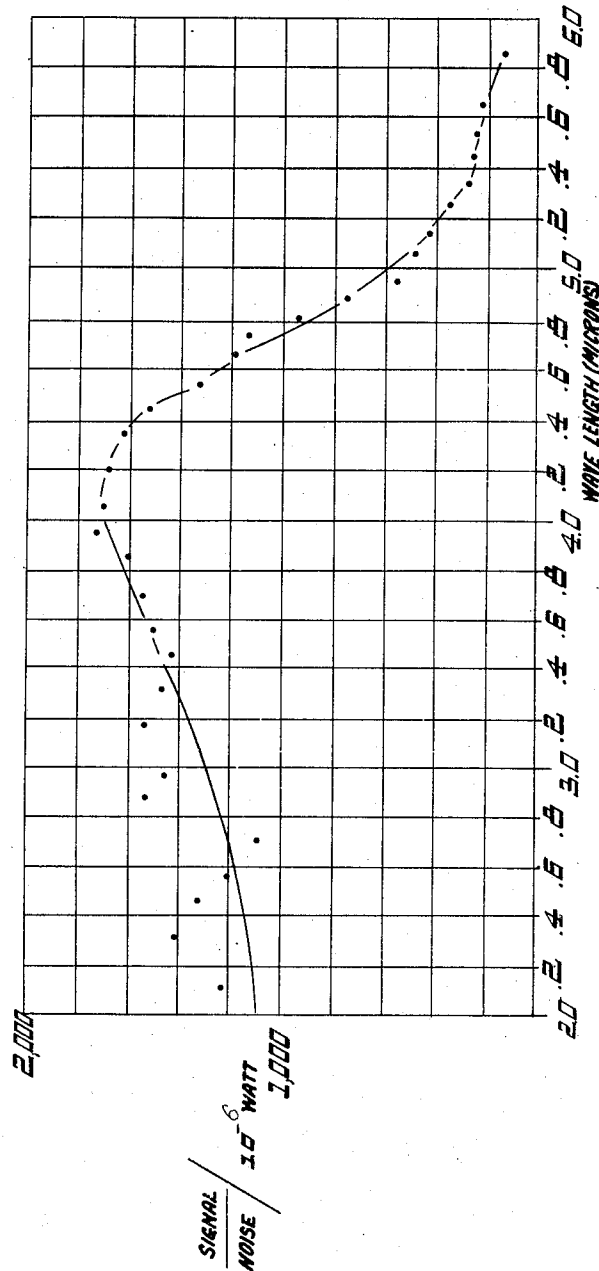


Fig. 12

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INFRA-RED SENSITIVE PHOTOCELLS

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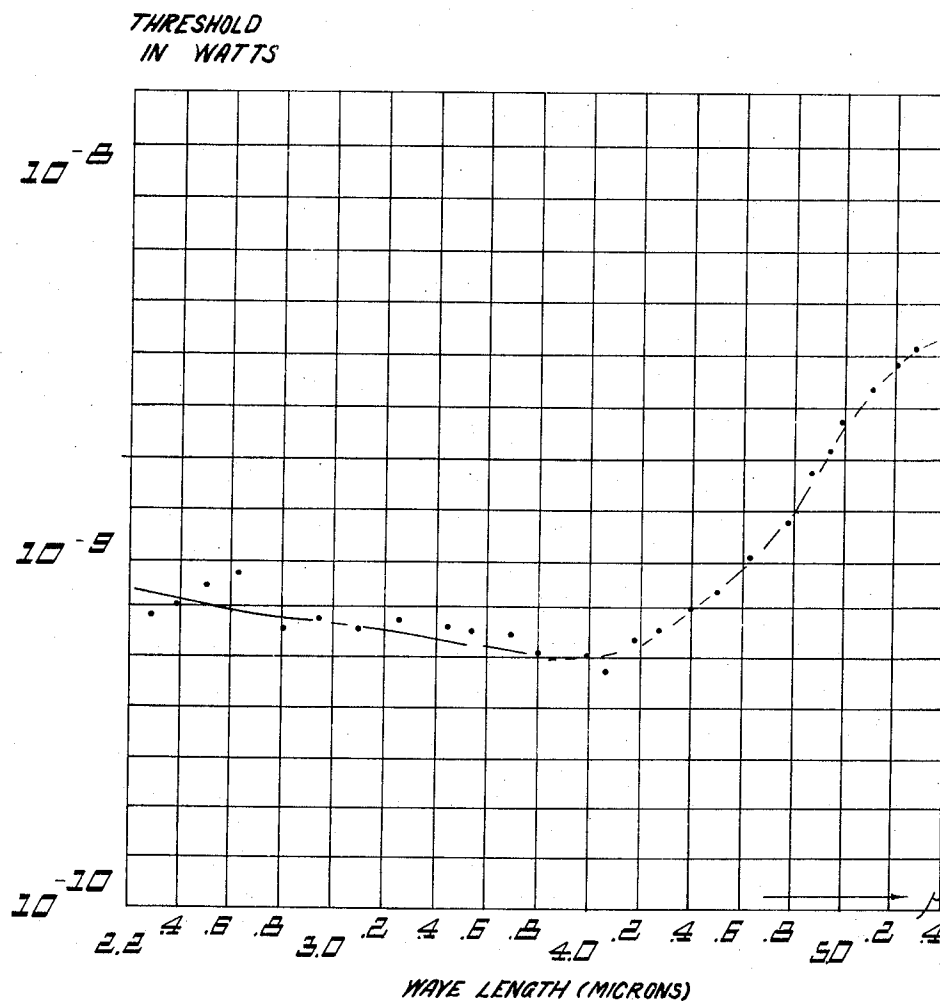


Fig. 13

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1

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INFRA-RED SENSITIVE PHOTOCELLS

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Application June 8, 1954, Serial No. 435,315

16 Claims. (Cl. 201—63)

This invention relates to improvements in infra-red sensitive photocells and more particularly to infra-red responsive photocells of the evaporated layer type and to methods of producing such photocells.

Infra-red responsive cells of the evaporated layer type have heretofore been produced as disclosed, for example, in U. S. patents to Cashman No. 2,448,516, "Photocell of Lead Sulfide," and No. 2,448,517, "Photocell of Thallous Sulfide." Infra-red responsive cells have also been discussed by L. Sosnowski, J. Starkiewicz and O. Simpson in "Nature," vol. 159, pages 818 and 819, June 14, 1947, and by O. Simpson and G. B. B. M. Sutherland in "Science," vol. 115, pages 1-4, January 4, 1952. Cells produced as described in the above mentioned publications are relatively unstable with low sensitivity and low signal-to-noise ratio, however, and the stability and performance of the cells have been found to be erratic during long term operation. Moreover, these prior methods of producing photocells are not adapted to produce cells having predetermined and reproducible characteristics, and this results in high production costs due to the high percentage of unsatisfactory cells.

It is, accordingly, a primary object of this invention to provide new and improved methods of producing photocells having improved response to infra-red radiation together with improved stability, high sensitivity, high signal-to-noise ratio and a low time constant.

Another important object of the present invention is the provision of improved infra-red responsive layers with a wider range of spectral sensitivity and lower "threshold" response.

Still another object is the provision of improved methods for producing such cells having predetermined characteristics and hence providing for relatively low cost mass production.

It is also an object of this invention to provide novel photocells having new and improved cell envelope and electrode structure.

Another object of this invention is to provide photocells having glass windows capable of transmitting infra-red energies of longer wavelengths than those heretofore disclosed.

These and other objects of this invention will become more fully apparent by reference to the appended claims and the following detailed description when read in conjunction with the accompanying drawings, wherein:

Figure 1 is a sectional view of a complete photocell;

Figures 2-9 are views of the components of the cell of Figure 1 and illustrates steps in the assembly of the components;

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

Figure 11 is a plan view of an electric oven and shows heating zones and a photosensitive cell in the heating zones;

Figure 12 is a graphical representation, by way of example, of the response curves of a typical lead telluride photocell under particular temperature conditions;

2

Figure 13 is a graphical representation of the variation of photocell "threshold" in watts as a function of the wavelength;

Figure 14 is a sectional view of an assembly for cooling a photocell; and

Figure 15 is a sectional view of a protective device for the thin glass window of a photocell.

With continued reference to the drawings, wherein like reference numerals are used throughout to designate like parts, Figure 1 shows a complete infra-red responsive photocell which comprises a cell envelope 20 fabricated of a suitable glass such as the sodium borate glass sold under the trade name "Duran" and manufactured by the Shott Glass Company in Germany. Envelope 20 includes an inner thimble 22 and an outer tubular shell 24 integrally connected with the thimble to define an annular chamber 26 therebetween. A layer 28 of radiation sensitive lead telluride is deposited on the top surface of the thimble, and lead wires 30 and 32, respectively, are connected to the sensitive layer 28 through electrodes 34 and 36. Lead wires 30 and 32 extend to the exterior of the envelope through the fused glass joint between thimble 22 and shell 24, and are of tungsten or other suitable material capable of being fused with and thus sealed to the glass of the cell envelope as at 38.

The upper end of the cell envelope is closed by a thin convex glass window 42. This window may be part spherical in shape as shown in Figures 1 and 3, and is made sufficiently thin to be capable of transmitting radiation within the range of response of the photosensitive layer. Other groups have reported the construction of infra-red sensitive cells employing lead telluride photosensitive areas, but have found it necessary to construct such units with sapphire (aluminum oxide) windows in order to permit the transmission of infra-red radiation of wavelengths up to 6 microns. These sapphire windows are very expensive and only small windows can be made because of the difficulty in preparing the material. With such small windows it often is impossible to collect the total infra-red radiation. We have found that thin glass windows of about 50 microns thick will also permit the transmission of infra-red radiation to 6 microns. In order to allow the windows to resist the possibility of breakage due to atmospheric pressure, we have made them of outwardly convex shape. This convexity of the extremely thin window admits a solid angle of about 90° and at the same time increases the resistance to breakage due to atmospheric pressure. By properly gauging the thickness and curvature of the cell windows, it is possible to produce cells allowing at least 60% transmission of infra-red radiation from 5 to 6 microns.

The cell envelope is formed in steps of taking a glass tube 40 (Figure 2) of suitable size, say of an external diameter of 30 mm. and wall thickness of about 1 mm., and an outwardly convex glass window 42 (Figure 3) having a mounting rim of a diameter approximately equal to that of tube 40, and fusing the abutting edges of the tube and window together to make the outer protective shell 24. Window 42 is preferably of the form and thickness described above, but its rim portion may be made of greater thickness to facilitate attachment of tube 40.

The inner glass unit or thimble 22 is formed of a glass tube 44 (Figure 4) having in this example an outside diameter of about 12 mm. and 1 mm. thick, and a glass disc 46 (Figure 5) which may be about 0.5 mm. thick and of a diameter of about 12 mm. Tube 44 and disc 46 are fused together to make the inner glass unit 22, and during this fusing operation the glass of the tube and disc may be molded to form integral bosses 45 on opposite sides of the thimble. The two lead wires 30 and 32 are enclosed within these bosses, with their ends embedded in disc 46 as indicated at 48 in Figure 6. The

glass is next ground to expose the upper ends of the wires as indicated at 50 in Figures 7 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 may cause noise and thus decrease the signal-to-noise ratio of the cell.

Electrically conductive material is next applied to the exposed tungsten lead wire ends to define electrodes 34 and 36 disposed as shown in Figure 9. It is important that these electrodes be parallel and of even width for best operation of the cell. The effective area of the sensitive material is measured between the two electrodes. We have found that the optimum area is 3×0.5 mm., but other areas may successfully be employed where necessary to suit the particular application.

The electrically conductive material of which electrodes 34 and 36 are formed preferably is aquadag, which is a colloidal graphite suspension in an aqueous or non-aqueous vehicle.

As shown in Figure 10 the thimble 22 and the outer protective shell 24 are assembled and sealed together, and a capillary tube 55 (Figures 10 and 11) is sealed into the envelope in communication with the chamber 26 therein. This tube may have an external diameter of about 6 mm. and an internal diameter of 1 mm. Tube 55 provides for the introduction of the lead telluride powder used in the production of the sensitive layer 28, and also for introduction of oxygen into chamber 26 and for exhausting gas from the chamber. The tube is removed and its entry point sealed off when formation of the cell has been completed.

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

We have found that lead telluride produced by any of the known laboratory methods is satisfactory for the production of photosensitive layers as hereinafter described. The sublimation of the lead telluride within the cell substantially eliminates any impurities that might adversely affect the operation of the photosensitive layer. We have used powder and single crystals obtained from different sources and of differing purity, and have found that satisfactory photosensitive layers may be produced from most of these lead tellurides regardless of the source or purity thereof.

One method for making lead telluride satisfactory for use in the photocells of this invention is to drop tellurium into molten lead at about 500°C . (reported by J. Margottet—*Recherches sur les Sulfures, les Seleniures, et les Tellurures Metalliques*, Ann. Ecole Normale, vol. 8, 1879, p. 247; or *Comptes Rendus*, vol. 84, 1877, p. 1293).

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

About 2 to 5 milligrams (depending on the cell size) of lead telluride powder or crystals, prepared in the manner described above or in other convenient manner, is passed into the chamber 26 of the cell through the tube 55, and is initially in Zone 1 indicated in Figures 10 and 11. The chamber 22 is now evacuated down to a pressure of 10^{-5} or 10^{-6} mm. of mercury. The lead telluride is next transferred from Zone 1 to Zone 2 indicated on Figures 10 and 11 by sublimation. To effect this transfer the cell is placed in a small oven such as shown at 57 in Figure 11. The temperature of the oven in region A should have a minimum value of 550°C . while the temperature in region B should be such that the temperature of the window does not exceed 100°C . to minimize dissociation of the lead telluride.

The lead telluride now at Zone 2 is transferred to the electrodes at Zone 3 by heating the window 42 to about 550°C . and at the same time cooling the electrodes with a stream of air through tube 62 directed at Zone 3. The cell is then cooled to room temperature. At this point

the resistance of the photosensitive layer should be of the order of 10^4 ohms.

The cooled cell in the oven is evacuated to about 10^{-5} or 10^{-6} mm. of mercury and heated to 250°C . When the cell has been heated to this temperature oxygen is introduced until the pressure in chamber 26 of the cell is of the order of 20×10^{-3} mm. of mercury. The resistance of the photosensitive surface is measured during the oxidation reaction. It will be observed during this oxidation process that the conductivity of the telluride layer decreases rapidly to a certain minimum. No further decrease in conductivity can be observed beyond this point. The cell must then be cooled quickly when this minimum conductivity point is reached. The cooling is accomplished by directing a stream of cold air on the lower end of the cell, then progressively moving the cold air stream along the cell towards the convex window. This procedure prevents condensation of dissociated tellurium on the photosensitive layer or on the window. The cell is then cooled to room temperature and again evacuated to 10^{-5} or 10^{-6} mm. of mercury. At this point control tests should indicate a cell resistance of the order 10^6 ohms. The cell is completed by flame sealing the capillary tube 55, close to the base of the cell.

To repeat, moisture must be excluded at all steps because while it may make the photosensitive material more sensitive under certain conditions, it makes the operation of the cell unpredictable.

In Figure 12 is shown the spectral sensitivity of a lead telluride cell prepared in the manner described hereinbefore. The cell was irradiated by a 300°C . black body having an emitting orifice of 1 sq. cm. area and placed at a distance of 80 cm. from the cell. The total incident energy impinging on the photosensitive layer was 0.24 microwatt, and was modulated at 400 C. P. S. so that the output of the cell could be measured at the output of an amplifier having a bandpass within the range of 50 to 5000 C. P. S. The biasing voltage across the cell layer was 50 volts and the cell was cooled with liquid air to a temperature of -180°C .

In the curve of Figure 12 the output response of this photocell is expressed in terms of its signal-to-noise ratio over the impinging energy (E) in microwatts, the cell response thus expressed being plotted as a function of wavelength of the impinging energy. Cell response was expressed in units of signal-to-noise/ 10^{-6} watt rather than in terms of absolute response because an indication of absolute response is of little practical value; the effective sensitivity of a photocell is determined by its signal-to-noise ratio at a particular wavelength and by the quantity of energy necessary to obtain this signal-to-noise ratio, rather than by absolute response. Figure 12 illustrates how the effective output response of the photocells of the present invention varies as a function of wavelength, and shows effective response to be peaked at approximately 4.1 microns.

Sensitivity of photocells may also be described in terms of their "threshold" of response, which is the minimum quantity of radiant energy impinging on the photosensitive layer which will produce an output signal equal to the noise ratio of the detector. "Threshold" may be defined either relative to the total radiation of all wavelengths from a black body of particular temperature, or relative to radiation of a specific wavelength or range of wavelengths. Photocells produced in accordance with this invention are characterized by a "threshold" response of about 3×10^{-9} watts when irradiated by a black body at 300°C ., and by a "threshold" response to radiation of particular wavelength which varies with the wavelength in the manner shown by the curve of Figure 14, wherein "threshold" in watts is plotted as a function of wavelength.

In Figure 14 there is shown one means for holding the lead telluride cell at a low temperature. The lead telluride cell 20 has a portion of the wall of thimble 22

5

treated to present a ground surface, as indicated at 65. A body 67 preferably of double wall construction, as in the familiar Dewar flask in which there is a vacuum in the space between the two walls, has a shank portion 69 providing a ground glass surface which may be inserted into the thimble 22, to make a tight fit with the surrounding ground glass portion 65 of the thimble. The body 67 also has a bowl portion 71 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 28 at the desired low temperature.

When the body 67 and the communicating interior of the thimble are filled with about 200 cc. of liquid air, the cell will operate at a temperature of about -180° C. for approximately one hour without recharging of the device with liquid air.

A protective device such as shown in Figure 15 may be employed to prevent breakage of the thin window 42, without adversely affecting the sensitivity of the unit. This protective device comprises a tubular shield member 73 held in position on the cell as by spring 75 fastened to shield member 73 and slidably engaging the exterior of the cell envelope 20.

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. An infra-red sensitive photocell comprising an envelope having an opening and providing an interior surface facing said opening; a photosensitive material on said surface responsive to infra-red radiation; and an outwardly convex thin glass window of approximately 50 microns thickness transparent to infra-red closing said opening.

2. An infra-red sensitive photocell comprising a tubular envelope closed at one end by a convex glass window of a thickness of the order of 50 microns and closed at the other end by a thimble upstanding within the envelope and having a closed end in spaced opposed relation to said window; electrodes carried by said thimble; and photosensitive material on the closed end of said thimble and conductively connected to said electrodes.

3. The photocell defined in claim 2 further comprising a window shield assembly including a tubular shield member adapted to partially enclose said envelope to protect said window against breakage.

4. The photocell defined in claim 2, including means for cooling said photosensitive material; said cooling means comprising a hollow body having a portion thereof removably secured in the open end of said thimble, and arranged cooperable with said thimble to define a reservoir for a cooling medium.

5. A photocell comprising an envelope, an upstanding thimble assembly in said envelope including a glass tube and a glass disc member, said disc member being sealed to the upper end of said tube by a fused joint therebetween providing a plurality of integrally formed boss members; a plurality of electrical conductors having portions thereof enclosed in said boss members and other portions thereof partially embedded in said disc member and partially exposed through the upper surface thereof; and photosensitive material on the upper surface of said disc member and conductively connected to said exposed portions of said electrical conductors.

6. The photocell defined in claim 5 wherein said envelope comprises an open ended tube having its one end sealed to said thimble assembly and its other end closed

6

by a convex glass window having a thickness of the order of 50 microns.

7. The photocell as defined in claim 6 wherein said photosensitive material is lead telluride.

8. The method of producing a photocell which includes the steps of providing an open ended glass tube and a glass disc member, heating one end of said tube and the disc member to effect a fused joint therebetween, deforming the glass adjacent said joint to form a plurality of integral glass boss members, embedding end portions of electrical conductors in said disc member adjacent the outer surface thereof and enclosing other portions of said conductors in said boss members, grinding the outer surface of said disc member to partially expose the electrical conductors embedded therein, positioning said tube within a larger tube, sealing said larger and smaller tubes together adjacent one end thereof, positioning an outwardly convex thin glass window over the other end of said larger tube, heating said larger tube and window to effect a fuse joint therebetween, applying electrodes to said ground surface of said disc member in contact with the electrical conductors exposed therethrough, and depositing photosensitive lead telluride on said disc member between and in contact with said electrodes.

9. The method defined in claim 8 wherein the step of depositing the photosensitive material on the disc member includes the steps of placing dry lead telluride in the space between said larger and smaller tubes, subliming said lead telluride and condensing the vapor on said thin glass window, heating said window to again sublime said lead telluride, condensing the vapor on the ground surface of said disc member in contact with the electrodes thereon, heating said cell and admitting oxygen thereto to sensitize the lead telluride, and when sensitization is complete cooling said cell and evacuating it.

10. In the method of producing a photocell in an envelope which has an outwardly convex thin glass window and contains an interior surface facing said window and provided with electrodes thereon, the steps which comprise placing dry lead telluride in the envelope; evacuating the envelope; then subliming said lead telluride and condensing the vapor on the thin glass window, heating said window to again sublime the telluride, and condensing the vapor to deposit a layer of telluride on and between the electrodes.

11. In the method defined in claim 10, the added steps of heating the envelope, introducing oxygen into said envelope and maintaining oxygen therein until the conductivity of the telluride layer has decreased approximately to a minimum, then rapidly cooling the envelope and again evacuating it.

12. In the production of a photosensitive cell in which heated material to be sensitized is in contact with electrodes within a heated envelope having a window adjacent said material, the method which comprises the steps of introducing oxygen into the heated envelope and maintaining the oxygen in said envelope until the conductivity of the photosensitive material approaches a minimum, then rapidly cooling the envelope and the sensitized material therein.

13. The method defined in claim 12 wherein the step of cooling the envelope is affected by the steps of directing a stream of coolant against the end of the envelope opposite its window, then progressively moving the coolant stream along the cell towards the window.

14. In the production of a photosensitive cell in which heated material to be sensitized is within a heated envelope having a window adjacent the material, the method which comprises the steps of sensitizing the material while heated, then rapidly cooling the envelope by directing a stream of fluid coolant against the end of the envelope opposite said window, and progressively moving the coolant stream along the cell towards the window.

15. In the production of a photocell in an envelope providing an interior surface having electrodes thereon,

the method which includes the steps of placing dry lead telluride in the envelope; evacuating the envelope; subliming the lead telluride and condensing the vapor to deposit a layer of telluride in contact with the electrodes; admitting oxygen into said evacuated envelope and maintaining oxygen therein until the conductivity of the telluride layer approaches a minimum, then rapidly cooling said telluride layer and again evacuating the envelope.

16. In the production of a photocell in an envelope providing an interior surface having electrodes thereon, the method which includes the steps of placing dry lead telluride in a first zone in the envelope; evacuating the envelope; subliming the lead telluride and condensing the vapor thereof in a second zone in said envelope; again subliming the lead telluride and condensing the vapor to deposit a layer of telluride on said interior surface in

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electrically conductive relation with the electrodes thereon; heating said envelope and admitting oxygen thereto to sensitize the lead telluride; and, when sensitization is complete, cooling the cell and evacuating its envelope.

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