Nov. 28, 1939. F. C. NIX 2,181,494

LIGHT SENSITIVE ELECTRIC DEVICE

Filed June 25, 1936 2 Sheets-Sheet 1

FIG. 1

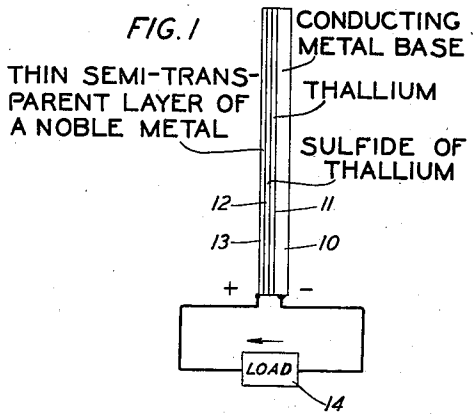

FIG. 2

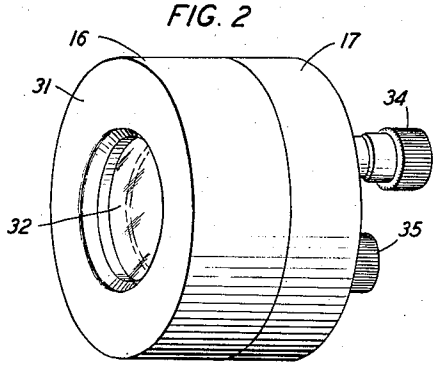

FIG. 3

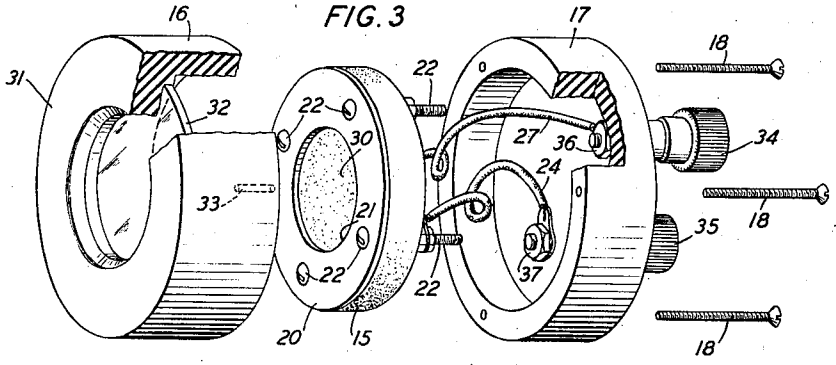

FIG. 5

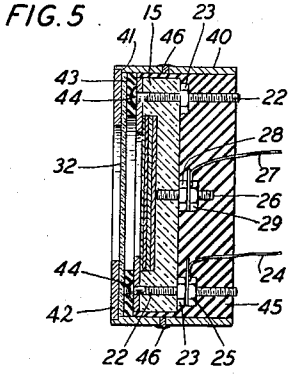

FIG. 4

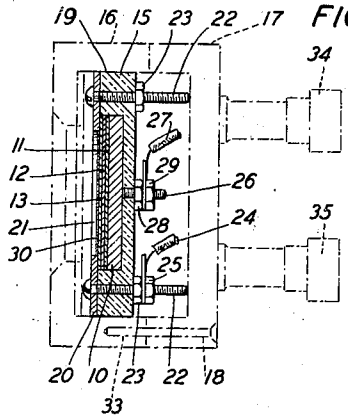

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FIG. 6

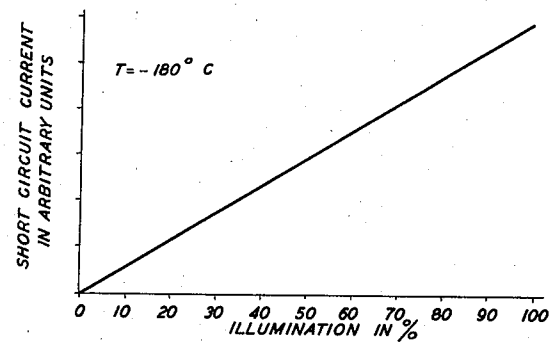


FIG. 7

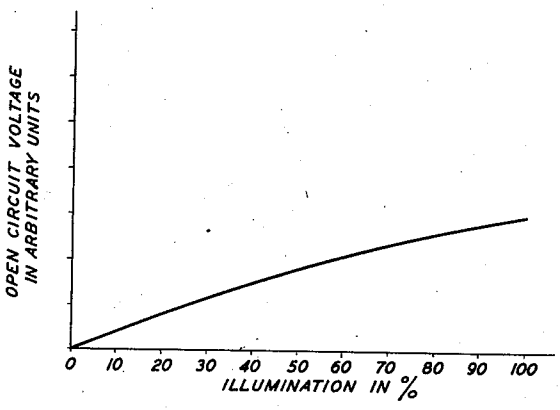


FIG. 8

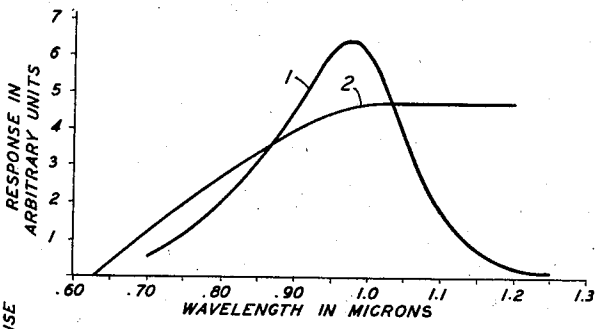
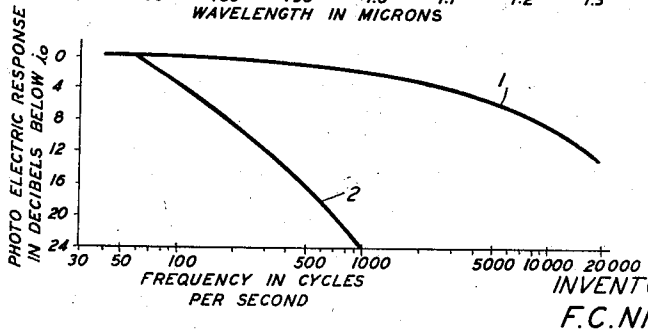


FIG. 9



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UNITED STATES PATENT OFFICE

2,181,494

LIGHT-SENSITIVE ELECTRIC DEVICE

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Application June 25, 1936, Serial No. 87,231

13 Claims. (Cl. 136—89)

This application relates to light sensitive electric devices and more specifically to photo-E. M. F. cells.

It is well known that when contiguous layers of certain materials, notably copper and copper oxide or selenium and a suitable conducting metal, are connected in an electric circuit and exposed to light an electromotive force will be generated without the use of a separate source of electromotive force in the circuit. Such light sensitive cells are generally known as photo-E. M. F. or photo-voltaic cells.

This invention is based upon the discovery that contiguous layers of thallium and thallium properly treated with sulphur provide a photo-E. M. F. cell having improved characteristics as compared with those of other known photo-E. M. F. cells. In the preferred arrangement the thallium is treated with sulphur to produce thallous sulphide and this is the form of cell to which the following description primarily relates.

A metal base may be provided for the thallium and a transparent conducting film for the thallous sulphide. The thallous sulphide is then exposed to light through the transparent film and contacts made to the cell through the transparent film and the metal base. This cell has been found to give a current response from a tungsten filament lamp or similar light source having a maximum spectral response in the red or infra-red which response is many times that obtained from any other known photo-E. M. F. cell. This cell also has other advantages which will be discussed more fully below.

One method of preparing such cells is by evaporating a layer of thallium upon a metallic base member, which may be, for example, nickel, removing the surface oxidation from the thallium layer by any suitable means such as by heating it in vacuum, exposing the pure thallium surface to a glow discharge in hydrogen sulphide (H_2S) to form a film of thallous sulphide on the thallium surface, cooling to room temperature, and then applying to the thallous sulphide surface a thin, semi-transparent auxiliary electrode of sputtered metal such as platinum. As a modification, thin discs of pure thallium may be used instead of evaporating the thin layer of thallium on a metal backing. As a further modification, the sulphurization process may be carried out by vaporizing pure flowers of sulphur instead of subjecting the thallium to a glow discharge in H_2S gas.

The invention may be more readily understood by referring to the following description taken in connection with the accompanying drawing forming a part thereof, in which:

Fig. 1 is a schematic diagram of a photo-E. M. F. cell of the type to which this invention is directed;

Fig. 2 is a perspective view of one of these cells in a suitable protecting cover;

Fig. 3 is an exploded view of the cell of Fig. 2;

Fig. 4 is a side view, partly in cross-section, of the cell shown in Fig. 2;

Fig. 5 is a side view, partly in cross-section of a cell having a different casing from that of the cell shown in Figs. 2 to 4; and

Figs. 6 to 9, inclusive, show characteristic curves of photo-E. M. F. cells of the kind described above and illustrated in Figs. 1 to 5.

Referring more particularly to the drawings, Fig. 1 is a schematic diagram of a thallous sulphide photo-E. M. F. cell. This cell comprises, in one embodiment, a metallic disc or base member 10 of any suitable rigid, conducting metal such as, for example, nickel or copper which serves as a conducting mechanical support for a layer 11 of thallium which is partially sulphurized to form a thin film 12 of thallous sulphide upon which is sputtered a semi-transparent conducting film 13 of a suitable metallic material such as platinum.

The only members necessary to produce the electromotive force are the thallium layer 11 and the thallous sulphide film 12 as the other two members are merely for the purpose of making electrical contact to the cell. It was observed in a large number of cells that a photo-E. M. F. effect was obtained by simply making contact with a platinum-pointed needle at points on the illuminated thallous sulphide surface before the sputtering of the platinum auxiliary electrode 13 upon this surface. These observations clearly show that the presence of the sputtered film is not essential to the observed photo-E. M. F. effect. The direction of flow of the photoelectrons in the cell during these observations was always from the thallous sulphide into the free thallium metal from which the thallous sulphide was obtained by sulphurization. The arrow in Fig. 1 indicates the direction of flow of the photoelectrons. An impedance such as, for example, that represented diagrammatically by the load 14 may be placed in the external circuit to control the current in that circuit.

The thallium layer may be a disc punched out of a thin sheet or it may be a thin film evaporated upon the metal base member 10.

Cells in accordance with this invention have been made as follows:

When the thallium was evaporated upon the nickel or copper base member disc, the process was carried out in an evacuated glass tube, the base member 10 being mounted within the tube. Pure thallium metal (the method of purifying the thallium will be described below) was placed in a suitable container within the tube from which it was evaporated onto the metal disc, heat being supplied to the container by an electric heating coil. A thin layer 11 of thallium was thus formed on the base member 10.

In some cases it has been found preferable to prepare the thallium in disc form rather than to evaporate a thin layer of thallium upon a base member. Thallium, which in its commercial form is usually in sticks or pellets, must be purified before it is suitable for use in these processes. The impurities, which are essentially oxide coatings, were removed by melting in vacuum and allowing the molten metal to flow through several constrictions about 0.03 inch in diameter, thus effectively straining out much of the oxide from the thallium and leaving it in a clean condition. The thallium in this form was melted in a reducing flame and allowed to flow into smooth flat bars, about $\frac{3}{8}$ of an inch thick. These bars were then rolled out into sheets about 0.021 inch thick from which the discs used in making the cells were punched. Care must be taken in rolling out the thallium sheets to avoid developing a flaky surface.

Whenever the discs were exposed to air, a thin layer of thallous oxide was immediately formed on the thallium. This film was removed by dissolving it in distilled water or dilute acid. The discs were then placed in a disc-shaped aluminum holder mounted in a horizontal position near the bottom of a vertically mounted tube for the sulphurization process. The process tube was immediately evacuated to prevent further oxidation. All of the remaining traces of oxide were then removed by heating. In general a temperature of 260° C. maintained for about two hours was found to be sufficient to clean up the discs.

If after the heat treatment the thallium had a bright, metallic luster it was ready for sulphurization. One method employed for sulphurizing the thallium was to expose it to a glow discharge in an atmosphere of hydrogen sulphide gas (H_2S) at a temperature of about 260° C. This temperature is not critical as sensitive cells have been made when the temperature was as low as 150° C. and as high as 280° C. These temperatures are both below and above the allotropic transformation point of thallium which is about 230° C. However, up to the present time a temperature of 260°±10° C. has produced the most sensitive cells. This temperature may be maintained by any suitable means, such as, for example, a cylindrical coil or furnace around the containing tube. The glow discharge took place between two perforated aluminum plates about ⅛ inch apart and located about ¼ inch from the disc and parallel thereto. The distance between the plates and the distance of the plates from the disc was chosen so as to bring the disc just within the region of the glow discharge so that a heavy concentration of sulphur atoms will be produced near the thallium. The H_2S gas was allowed to flow through the tube continuously at a rate which would maintain a gas pressure of about 1.3 millimeters of mercury. The voltage impressed on the perforated aluminum plates was about 390 volts. This gave a discharge current of 29 milliamperes for the given pressure and size of plates. The time of exposure to the discharge for best results was about three minutes.

A second method of sulphurizing the thallium consists in vaporizing flowers of sulphur (preferably degassed) to produce sulphur vapor and allowing the sulphur vapor to pass into the process tube wherein the thallium disc or layer is mounted. Before being used in the process, the sulphur may be boiled in vacuum and vaporized to remove all impurities. The side tube in which the purified sulphur was placed was joined to the process tube at a point intermediate the ends thereof. The process tube was evacuated and then the thallium disc or layer was heated to a temperature of 260°±10° C. and this temperature maintained throughout the sulphurization process. The sulphur was then heated to a high enough temperature to cause it to boil and the sulphur vapor thus allowed to flow into the process tube and sulphurize the thallium, producing a film of thallous sulphide. Some typical cells which have been made by one or the other of the processes stated above have been tested to determine chemically the composition of the thin film produced by the sulphurization. In all cases the film was found to comprise Tl_2S (thallous sulphide). Possibly some additional sulphur may be present in the film, either as free sulphur or in the combined state as thallic sulphide (TlS).

The appearance of the thallium surface rapidly undergoes numerous changes as its treatment with sulphur progresses. First, a very thin, translucent black layer is formed. Addition of a small amount of sulphur to the unit in this state results in a sudden change such that the color of the surface becomes a dark gray. This is believed to be the most sensitive condition. By substantially increasing the quantity of sulphur introduced into the reaction chamber a violent reaction may be precipitated causing the surface to melt and then immediately solidify. In instances in which excessive amounts of sulphur were used a crystalline surface was obtained. The most sensitive cells were found to be those in which the surface had not melted. Those cells in which the surface had become molten in spots during the sulphur treatment were found to have high sensitivity but somewhat lower than the maximum sensitivity obtained from those of the preceding group. Use of slightly greater quantities of sulphur such that the reaction was stopped immediately after the entire surface of the cells melted resulted in the production of cells of lower sensitivity. Still lower sensitivity resulted when sulphurization was heavy enough to give crystalline surfaces.

Both methods of sulphurization described above have been found suitable for preparing these cells as by both methods it is possible to maintain a constant and uniform sulphur concentration at the surfaces to be sulphurized and to permit sulphurization to continue for accurately controlled periods of time under reproducible conditions. It will be understood, however, that any other suitable method for partially sulphurizing the thallium may be used. In comparing the two methods, in general, the hydrogen sulphide glow discharge method is susceptible to more accurate control while the sulphur vaporization method is quicker and requires simpler apparatus.

After sulphurization the evacuated system is allowed to cool to room temperature at which

time the unit is removed and receives a thin auxiliary electrode of sputtered platinum. Gold is also a suitable substance for this auxiliary electrode. The semi-transparent conducting auxiliary electrode 13 serves as the front electrode, and the metallic supporting disc 10 constitutes the back electrode. The completed cells may then be placed in an evacuated glass vessel in order to protect them from changes in atmospheric conditions. The cells have proven to be quite stable over an observation period of several months.

Vacuum is not necessary to the successful operation of the completed photo-E. M. F. cell herein described, but some container or casing is necessary in order to protect the cell from changes in atmospheric conditions such as, for example, an excess of water vapor in the air. Such a casing may be evacuated if desired. Two typical casings will be described below.

Figs. 2, 3 and 4 show by way of example a thallous sulphide photo-E. M. F. cell in a typical molded container. Fig. 2 shows the completely assembled cell, Fig. 3 is an exploded view of the cell and Fig. 4 shows the cell in cross-section. The complete assembly comprises a cell unit member 15, a front cover 16 and a back cover 17 together with means such as the screws 18 for connecting the parts together. The cell shown in Fig. 1 comprising the base member 10, the thallium layer 11, the thallous sulphide film 12 and the semi-transparent platinum layer 13 may be set in a casing of molded ceramic material 19 on which may be placed a brass cover plate 20 having an opening 21 therein. The brass plate 20 is fastened to the ceramic material 19 by any suitable means such as the screws 22 and nuts 23. The plate 20 may be slightly concave so that it forces the elements of the cell unit in close contact relation with each other. A contact lead 24 may be connected to the screw 22 by nuts 23 and 25 to form a front contact lead. The screws 22 also act as spacers in the assembly of the complete cell. The rear contact is made by a screw 26 which makes electrical contact, through the ceramic material 19, with the base member 10. The contact lead 27 may be connected to the screw 26 by any suitable means, such as by nuts 28 and 29. To protect the unit from changes in humidity a thin coating 30 of a wax-like substance may be provided for the transparent metallic layer 13. This coating 30 is placed in the aperture 21 of the plate 20 and is transparent. Ozokerite wax and paraffin are satisfactory waxes for this purpose.

The front cover 16 for the cell unit 15 may comprise a casing 31 of molded material such as, for example, Bakelite, having a glass window 32 in front of the opening 21 in the metal plate 20. The casing 31 is adapted to completely enclose the cell unit 15 with the exception of the ends of the screws 22 and is provided with threaded holes 33 to receive the screws 18.

The back cover member 17 comprises a casing which is preferably of the same material as that of the front casing 31. It is provided with binding posts 34 and 35 which terminate in screws 36 and 37 on the inside of the back casing member. The contact lead 27 is adapted to be connected to the screw 36 and the contact lead 24 is adapted to be connected to the screw 37. Screws 18 pass through holes in the casing 17 and hold the front and back members in close engagement with each other, thus completely enclosing the cell unit 15. The screws 22 which rest against the inner surface of the back cover 17 press the cell unit 15 close to the glass 32. When the device is assembled as described above, a change in the light intensity incident upon the glass member 32, and through this member upon the cell unit 15, will produce a difference of potential between the binding posts 34 and 35.

Fig. 5 shows a thallous sulphide cell having a metal container. This container comprises a metal cylinder 40, of suitable material such as brass, having a shoulder 41 at one end. A brass ring 42 rests on this shoulder and is fastened to the cylinder 40 by any suitable means such as solder. Against the ring 42 is placed the glass disc 32 which is sealed into the cylinder by any suitable means such as by "Picien", a commercial form of sealing wax. A hard rubber ring 43, having holes or indentations 44 to fit around the heads of the screws 22 and hold the unit 15 in place in the cylinder 40, is placed against the surface of the glass disc 32. The unit 15 may be the same as disclosed above in Figs. 2 to 4, inclusive. The inside of the cylinder is then filled with "Picien" wax thus enclosing the unit 15. The leads 24 and 27 extend through the wax for contact purposes. A hole 46 may be drilled in the cylinder 40 before the cell is assembled so that when the wax is poured in there is a passage for the escape of air. This hole is sealed after the wax is poured by any convenient means such as solder. In the metal case cell, the coating 30 of Ozokerite or other wax may not be necessary.

Measurements on cells similar to those described above at temperatures varying from room temperature down to the temperature of liquid air have shown that the short-circuit current resulting from exposure to the radiation of an incandescent tungsten lamp is substantially proportional to the incident light intensity at all temperatures. Fig. 6 shows the characteristic short-circuit current versus per cent illumination of a cell at −180° C., the unfiltered light standard being taken as 100% and filters being used to produce the other intensities incident upon the cell.

Fig. 7 shows the open circuit voltage versus per cent illumination of a typical one of these cells. This characteristic departs from the linear form at higher percentages of illumination but the curvature is not serious. Many cells have been made in which this characteristic is also linear. The curves shown in Fig. 6 and Fig. 7 are typical of results obtained on a large number of cells.

The short-circuit current yield from cells of this type has reached, in some cases, as high as 5000×10^{-6} amperes per lumen, but the average yield of a cell is somewhat less than this. These measurements were made by exposure to the radiations from a light source having a maximum energy emission in the region of red and infrared such as, for example, an incandescent tungsten lamp. This short-circuit yield of 5000 microamperes per lumen may be compared with a yield from cuprous oxide front and back wall cells of 150 and 15 microamperes per lumen respectively, and a yield from selenium photo-E. M. F. cells of about 450 microamperes per lumen.

The open circuit voltage produced by cells of this type from a light source of approximately 0.37 lumen has reached a value as high as 0.17 volt. The average from this light source was found to be around 0.11 volt. These figures compare very favorably with the selenium photo-

E. M. F. cell and are much larger than those of the cuprous oxide cells, both front and back wall types.

Curve 1 of Fig. 8 shows a typical equi-energy spectral response curve of a thallous sulphide photo-E. M. F. cell. Curve 2 of this figure shows a typical transmission curve of thallous sulphite film on glass. This latter curve is included in order to show the relationship between optical absorption of the thallous sulphide and the spectral photo-response of the thallous sulphide cell.

Curve 1 of Fig. 9 shows the photoelectric output of a thallous sulphide photo-E. M. F. cell as a function of the frequency of interruption of the incident light up to 20,000 cycles per second. This curve shows the decrease in current response in decibels with an increase in frequency. The data for a selenium photo-E. M. F. cell is given in curve 2 of this figure in order to permit a direct comparison to be made between this characteristic of the two cells. As may be seen from the two curves, the thallous sulphide photo-E. M. F. cell possesses vastly superior properties at high frequencies to the selenium photo-E. M. F. cell or for that matter to any other known photo-E. M. F. cell.

Careful measurements were made in order to ascertain whether rectification occurred in the cell such as is found in most cuprous oxide and selenium photo-E. M. F. cells. Some of these cells produce slight rectification while others do not, the rectification effect apparantly being present in cells having relatively thick thallous sulphide layers. As pointed out above the cells having very thin thallous sulphide layers were found to give the best photo-E. M. F. response. These results tend to indicate that the rectification phenomenon is not to be considered as a necessary accompaniment to the photo-E. M. F. effect although both effects may exist in the same cell.

The cells have internal resistances of from 20 to 1500 ohms but this resistance appears to be substantially independent of the intensity of illumination. The cells cannot therefore be considered as photoconducting.

It will be apparent that this thallium photo-E. M. F. cell possesses many advantages over other known photo-E. M. F. cells. Various modifications may obviously be made without departing from the spirit of the invention, the scope of which is defined by the appended claims. In the claims, the word "layer" is intended to be broad enough to cover the arrangement wherein the thallium disc is used.

What is claimed is:

1. A photo-E. M. F. cell comprising a metal base a thallium member adjacent to and in contact with said metal base, and a film of thallous sulphide on the face of said thallium member remote from the base.

2. A photo-E. M. F. cell comprising a metal base, a thallium layer deposited on said base so as to be integral therewith, and a film of thallous sulphide on said thallium layer.

3. A photo-E. M. F. cell comprising a metal base, a thallium layer on said base, a film of thallous sulphide on said thallium layer, and a semi-transparent electrically conducting layer of a noble metal on said thallous sulphide.

4. A photo-E. M. F. cell comprising a base of conducting metal, a thallium layer on said base, a film of thallous sulphide on said thallium layer, and a thin film of a noble metal on said thallous sulphide.

5. The method of preparing a thallous sulphide photo-E. M. F. cell comprising the steps of sulphurizing a layer of thallium until the surface of the thallium attains a dark gray color, and applying a thin light-conducting layer of a noble metal to said sulphurized layer.

6. The method of preparing a thallous sulphide cell comprising the steps of evaporating a film of thallium upon a metallic member, exposing the thallium surface to a glow discharge in H_2S gas to form a film of thallous sulphide on said thallium surface, cooling to room temperature, and applying to said thallous sulphide surface a thin semi-transparent electrode of a noble metal.

7. The method of preparing a thallous sulphide cell comprising the steps of sulphurizing a thallium disc by exposure to sulphur vapor in a temperature of approximately 260 C. to form a film of thallous sulphide on said thallium surface, cooling to room temperature, and applying to said thallous sulphide surface a thin semi-transparent electrode of a noble metal.

8. The method of preparing a thallous sulphide photo-E. M. F. cell comprising the steps of sulphurizing a layer of thallium involving the application of heat until the surface of the thallium attains a dark gray color, cooling to room temperature, and then applying to said sulphurized layer a conducting electrode of a noble metal.

9. The method of preparing a thallous sulphide cell comprising the step of sulphurizing a thallium member by exposure to sulphur vapor at a temperature within the range from 250° C. to 270° C. to form a film of thallous sulphide on said thallium.

10. The method of preparing a thallous sulphide cell comprising the steps of sulphurizing a thallium member by exposure to sulphur vapor at a temperature within the range from 250° C. to 270° C. to form a film of thallous sulphide on said thallium surface, and then cooling to room temperature.

11. The method of preparing a thallous sulphide cell comprising the steps of sulphurizing a thallium member by exposure to sulphur vapor at a temperature within the range from 250° C. to 270° C. to form a film of thallous sulphide on said thallium surface, cooling to room temperature, and sputtering on said thallous sulphide surface a thin semi-transparent electrode of a noble metal.

12. A photo-E. M. F. cell comprising a metal base, a thallium member adjacent to and in contact with said metal base, and a film of a material comprising thallium and sulphur on the face of said thallium member remote from the base.

13. A photo-E. M. F. cell comprising a metal base, a thallium member adjacent to and in contact with said metal base, and a film of a sulphide of thallium on the face of said thallium member remote from the base.

FOSTER C. NIX.