

Jan. 5, 1937.

A. CHRISTY

2,066,611

SELENIUM CELL

Filed Dec. 10, 1932

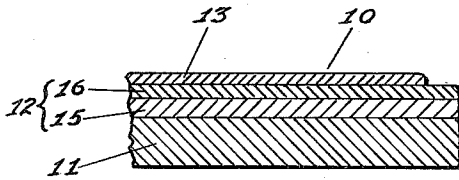


*Fig. 1.*

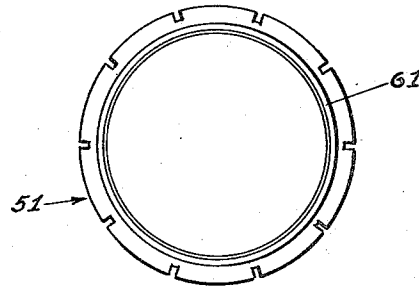


*Fig. 3.*

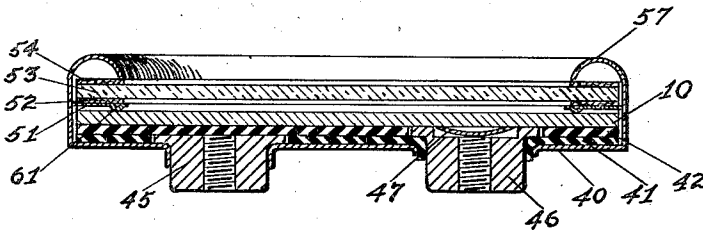


*Fig. 2.*

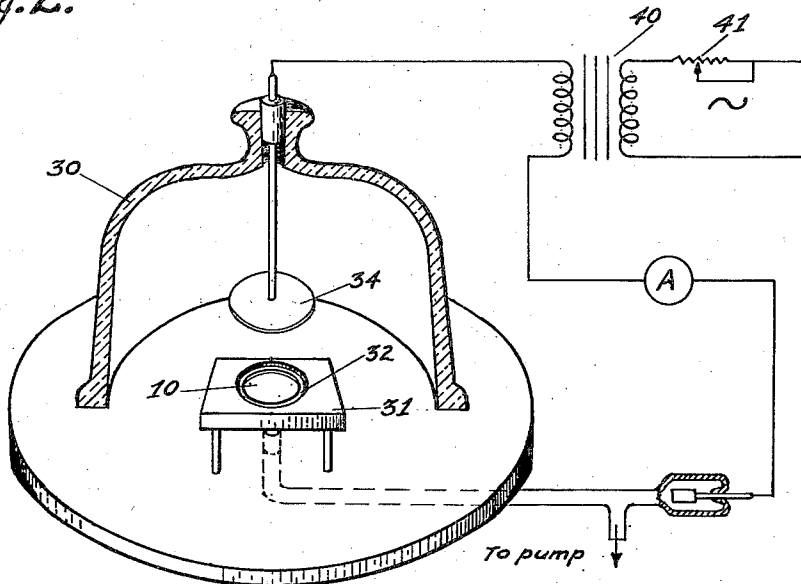


*Fig. 4.*

Inventor  
Andrew Christy  
By: Mueller & McLaughlin  
Attys.

## UNITED STATES PATENT OFFICE

2,066,611

## SELENIUM CELL

Andrew Christy, Chicago, Ill., assignor to G-M Laboratories, Inc., Chicago, Ill.

Application December 10, 1932, Serial No. 646,627

6 Claims. (Cl. 136—89)

The present invention is related generally to light sensitive electro-responsive devices, and more particularly to photo-voltaic cells of the dry or electronic type.

5 In many applications of light sensitive devices, such as portable photometers and the like, it is desired to employ a cell that requires no source of energy for its operation other than the light to which it responds.

10 A cell for such a purpose should have an internal resistance which is comparatively low so as to permit its ready adaptability for use with ordinary electrical instruments of the portable variety. It should furthermore be of sufficiently rugged construction to withstand a considerable amount of ordinary use and abuse.

It is known that certain semi-conductors are capable of generating an electric current when illuminated. Among these are selenium, molybdenite ( $\text{MoS}_2$ ), argentite ( $\text{Ag}_2\text{S}$ ), acanthite ( $\text{Ag}_2\text{S}$ ), cuprous sulphide ( $\text{Cu}_2\text{S}$ ), cuprous oxide ( $\text{Cu}_2\text{O}$ ), lead sulphide ( $\text{PbS}$ ) and diamond.

According to my present invention I apply a thin coating of a light sensitive material to a base member, the material being held in place by an adhesive substance which is also sufficiently conducting to establish a good electrical connection therewith. Over the light sensitive material I apply a light-permeable contact means which preferably takes the form of a transparent film of silver. The light may then pass through the silver layer to irradiate the sensitive material and thereby generate an electric current and/or a difference of electric potential between the two conducting layers which constitute the terminals of the cell.

Preferably I employ selenium as my light sensitive material because it possesses the desired light sensitive property to a marked degree, because it may be easily applied to a base and formed into a thin layer, and because its compounds with certain metals, that is, certain selenides, have the desired adhesive properties for holding the selenium to its supporting base, and are also relatively good conductors.

An object of the present invention is to provide a light sensitive cell which is capable of delivering a substantial amount of the electrical energy independently of any external power supply.

A further object is the provision of a selenium cell of low internal resistance.

55 A further object is the provision of an improved light sensitive cell.

A still further object is the provision of a method of manufacturing such cells.

Other objects and advantages will appear as the description proceeds.

In order to obtain an understanding of the teachings and the practice of the present invention, the following description is to be taken in connection with the accompanying drawing which forms a part of this specification and in which:

Fig. 1 illustrates diagrammatically, a section through a light sensitive cell, or cell plate of my present invention;

Fig. 2 illustrates a completed cell;

Fig. 3 is a detail thereof; and

Fig. 4 is a more or less schematic illustration of certain apparatus used in the manufacture of the cell plate of my present invention.

Referring to Figure 1, the reference numeral 10 indicates a light sensitive cell or cell plate consisting of a metal plate 11 carrying a coating 12 of light-sensitive material over which there is provided a thin metal film 13 which is pervious to light—such as a thin silver coating. The coating 12 of light-sensitive material comprises essentially a layer 15 of a selenide next to the plate 11 and a layer 16 of metallic selenium thereover. It will be apparent that Figure 1 is not drawn to scale, but that certain dimensions have been exaggerated for purposes of illustration.

Referring to Fig. 2, a cup shaped casing 40 contains a pair of insulating disks 41 and 42. A terminal stud 45 has a non-circular head which fits snugly into a perforation in the disk 41, and its shank extends through and makes electrical contact with the base of the cup 40. A second terminal stud 46 has its head fitted into the insulating disk 42 and its shank extending through the disk 41 and the bottom of the cup 40. The disk 41 is embossed so as to insulate the terminal stud 46 from the cup 40, while the disk 42 lies over the head of the stud 45 to insulate it from the lower side of the cell plate 10.

A recess in the head of the stud 46 contains a resilient contact piece 47. The completed cell plate 10 lies against the disk 42 with its sensitive surface facing the open end of the cup and its base plate 11 making electrical contact with stud 46 through the contact piece 47. A formed contact ring 51, a paper washer 52, a glass plate 53 and a second paper washer 54 are stacked on the cell plate assembly 10. The upper edges 57 of the cup 40 are turned over to bear against the washer 54 so as to clamp the assembly tightly together.

The contact ring 51 is provided with a bead 61 which presents a smooth face to the silver surface 13 of the cell plate 10 to engage the same along the entire length of the bead. Good electrical contact is thereby assured without danger of cutting or otherwise injuring the extremely thin silver film. The ring 51 is arranged to make peripheral contact with the walls of the cup 40 and to that end it has a diameter slightly greater than that of the cup and is adapted to be forced into place. As is shown in Fig. 3, a flat annular portion at its outer edge is slitted radially to weaken its resistance against the deformation incident to its being forced into place, while a continuous annular portion is left at each side of the bead 61 to provide strength to resist crumpling there. The bead is however, sufficiently resilient to insure a permanent good electrical connection between the silver surface 13 of the plate 10 and the ring 51.

In constructing the cell plate 10, according to one manner of practicing the invention, the metal plate 11 is first boiled in a caustic solution to thoroughly clean it after which it is rinsed and then etched by dipping it in acid. I prefer to employ a hydrochloric acid solution of high concentration having a small amount of nitric acid added thereto.

I may next place the etched plate in a vacuum chamber, and heat it to a high temperature while evacuation is maintained. This serves to remove any absorbed or adsorbed gases and vapors from the plate so as to prevent their exudation during subsequent stages of manufacture with consequent harmful effects to the light sensitive coating. Evacuation should be maintained until the plate cools.

The plate is then heated to a temperature somewhat above 217 degrees centigrade, care being exercised to prevent deterioration of the surface. The plate may either be heated quickly in air as by placing it on a hot-plate or it may be heated in a non-oxidizing atmosphere. The hot-plate may be conveniently employed both for heating the plate 11 and for maintaining it at the proper temperature during the subsequent application of the selenium.

As is well known, selenium may assume various allotropic forms, among which are the gray metallic and the vitreous form. The gray metallic form is the only one which is sensitive to light. All other forms tend to change to the metallic state, the process being accelerated by a rise in temperature, and at temperatures above 217 degrees centigrade, the melting point of the metal, selenium ordinarily exists only as a metal.

If molten selenium is cooled rapidly, that is, without annealing, it goes into the vitreous state and remains plastic at temperatures as low as 60 or 70 degrees centigrade. However, it returns more or less readily to the metallic or crystalline condition upon being annealed, the time required for the change being dependent upon the temperature employed.

In the construction of my cells, I preferably use selenium which has been purified by distillation. It is taken from the still in the metallic state and crushed. This crushed metallic selenium is then applied to the heated metal plate 11 where it melts. However, it may be applied to the plate 11 in either the vitreous or the molten state if desired. The molten selenium is kneaded into the plate 11 by means of a pallet knife or glass rod, or any other suitable device to bring it into intimate contact with the metal plate so

that it will easily re-act therewith to form the thin uniform layer 15 of selenide next the plate. The kneading also works out any air bubbles that might be present in the molten metal. The etching of the surface of the plate 11 as described above, contributes materially to the final uniformity of the selenide layer 15.

The plate 11 may be composed of any metal which reacts slightly with selenium to form a selenide such as iron, nickel, cobalt, tin, lead or copper. I prefer to use the commercial grade of iron known as "hot rolled, low carbon, mild steel". Of the above metals, copper and lead react most readily with the selenium, and when the plate 11 is composed of either of these, the selenium layer 16 must be quite thick in order to insure that no minute protuberances of the selenide layer 15 penetrate the overlying metallic selenium stratum 16 to make contact with the silver electrode 13. Selenium has a low conductivity and therefore a thick layer of selenium metal is objectionable because it increases the resistance of the cell. On the other hand the selenides have comparatively good conductivities so that any selenide reaching through to the silver will tend to short circuit the cell. Iron, nickel, cobalt and tin react with selenium to form a thin layer of selenide next to the plate of such a character that it can be completely covered with a selenium layer a few thousandths of an inch thick, whereas, a copper or lead plate must be covered with a much thicker coating of selenium.

I may under certain conditions plate a very thin layer of copper on a base of a less active metal such as iron by immersing the latter in a saturated solution of copper sulphate for two or three seconds, to deposit a copper coating thereon less than 0.0001 inch thick. The molten selenium will then have only a limited amount of copper with which to combine, and selenides of both iron and copper will form. Such a copper coated plate, because of the limited quantity of copper selenide that may be formed, will make a satisfactory cell when covered with only a thin layer of selenium. Lead or a mixture of tin and lead coated onto an iron plate by a "tinning" process will similarly give satisfactory results.

The presence of some selenide is desirable both for furnishing a good electrical connection between the plate and selenium and for holding the selenium metal to the plate. Furthermore, the results of numerous tests of finished cells have indicated that the selenide may be actually essential to the generation of an electric current and/or voltage by the cell. That is, it appears that a cell constructed so as to have no selenide layer would be incapable of delivering a current to an external circuit independent of other sources of electromotive force. It also appears that the property of rectification is necessary, though not sufficient, for the successful operation of a cell. That is, a good cell will present a higher resistance in one direction than the other when an external voltage is applied to its terminals.

Thus experimental cells which I have constructed using certain grades of iron for the plate 11 which appeared to react very little with the selenium, would deliver no appreciable current to an external circuit. These cell-plates were then bent to chip off the selenium coating and the surface resistivity of the under surfaces of the selenium flakes was measured. In all these cells this resistivity was found to be high as compared

with the resistivities measured similarly on the under surfaces of selenium flakes taken from good cells, that is cells which would deliver a current to an external circuit when illuminated. Since the selenides have a lower resistance than selenium itself, these measurements are interpreted as indicating the absence of the selenide in the poor cells.

It is believed that the irradiation of the selenium does not in and of itself induce or generate an electric current or voltage of the order of magnitude obtained from these cells in any particular direction, but that on the contrary it induces a more or less random electronic activity which is modified or controlled by the rectifying characteristic of the cell so that a unidirectional current or voltage is developed which may be utilized in an external circuit.

The application of the selenium to form the selenide layer may be made at any temperature above 217 degrees, the melting point of selenium metal, though it should preferably be kept below 300 degrees centigrade. A second quantity of selenium is then melted onto the plate preferably at a temperature of about 220 to 240 degrees centigrade. These temperatures should not be greatly exceeded because at higher temperatures the selenium metal sublimes rapidly causing bubbles to appear in the finished selenium coating. The entire quantity of selenium might under certain conditions be applied at once, or at a different temperature than I have given, but I have found that the above procedure insures the formation of a selenide layer next the plate having the character required for a high quality cell of the present type.

The coated plate is next cooled at a sufficiently rapid rate to bring the selenium to the plastic vitreous condition and the coating is then pressed to the desired thickness. The temperature at which the pressure should be applied depends somewhat upon the amount of pressure available and it should be applied while the selenium is sufficiently plastic to permit it to be pressed out into an even surfaced, uniform layer.

In order that the selenium layer may better retain its surface after being formed in the press, it is desirable to have the pressing operation carried out at a low temperature. Preferably the temperature should not go below 140 degrees, for if it does the body of selenium may gain sufficient rigidity so that strains will be set up in the material as a result of forming it under pressure. These strains may then cause the material to crack when it is later annealed.

The coated plate is placed on the bed of the press, which may be kept at a substantially constant temperature of about 140 degrees centigrade, and the viscosity of the selenium surface may be tested from time to time. When the selenium reaches the desired condition, an even surfaced plate or pressing block having a temperature of about 140-180 degrees centigrade is laid over the selenium and the pressure applied until the selenium and selenide are pressed to the desired thickness, preferably about 0.002-0.006 inch. Suitable stops may be provided on the bed of the press to engage the surface of the pressing block so as to determine the thickness of the pressed coating. As was suggested above, it is desirable to have the light sensitive coating of selenium as thin as possible in order to decrease the resistance of the cell. However, the layer must not be so thin that slight irregularities in the selenide layer may protrude through the

selenium to make contact with the silver electrode layer. It is therefore apparent that the regular and uniform character of the selenide layer is of great importance in that it permits the sensitive layer to be pressed to as small a dimension as is warranted by the precision of the pressing operation.

The pressing block may be composed of, or faced with any suitable material, such as glass, mica, high carbon steel, aluminum, chromium or the like, which presents a hard even surface to the selenium but does not react therewith or permanently adhere thereto. In order to insure that the selenium will not react with the pressing block, oil may be applied to the face of the block and subsequently wiped off with a cloth leaving a thin invisible oily film on the surface of the block. To insure proper annealing of the selenium film the face of the block may be roughened, as by sand blasting if glass, or sand papering if metal, so that the minute irregularities of the roughened pressing block surface will be impressed into the surface of the selenium to serve as nuclei for the even crystallization of the selenium layer.

As a result of the comparatively rapid cooling prior to, and during the pressing operation, the selenium is in the vitreous or plastic condition when pressed. It must next be removed from the press, leaving the pressing block in place on the cell plate, and be annealed at some temperature between 150 and 200 degrees, preferably at about 170-180, long enough for complete crystallization of the selenium to take place. This will require from five to thirty minutes. The pressing block may be removed as soon as this annealing is completed for when the surface of the selenium crystallizes it no longer sticks to the block. When the annealing is complete the temperature is gradually reduced to room temperature over a period of several hours.

It may happen that the selenium metal does not assume the desired crystalline formation in being annealed only once, and repeated annealings will be required to secure the desired results. The condition of the selenium can be determined by experiment from the appearance of its surface. The coating will generally be in the best condition when its surface is the least mirror-like. However, the character of the surface of the pressing block usually has a greater effect on the appearance of the selenium surface than does the condition of crystallization. I therefore prefer to press out and anneal a large number of cells with one block and then make direct comparisons of the surfaces of the several cells. A few of these may even be selected and finished so that their final sensitivities may be used as an indication of the condition of the unfinished cells. The cell should not be reannealed after its silver electrode has been put on as a reaction occurs between the silver and selenium when heated which impairs the sensitivity.

The annealed plate is next mounted in an evacuating chamber 30 as shown in Fig. 4, with its coated face up. It is preferably laid in a recess in a heavy metal block 31 and a mask 32 is placed over it so as to cover its exposed edges.

A silver electrode 34 is suspended over the plate 32 and another electrode 35 is situated remotely therefrom. Preferably the electrode 35 is included in a tubing system communicating with the chamber and is at such a distance from the chamber as to preclude the possibility of any metal from the electrode 35 reaching the cham-

ber itself. The tubing also communicates with a suitable evacuating pump.

The two electrodes 34 and 35 are connected to a high voltage winding of a transformer 40, the primary winding of which is connected to a suitable alternating current supply and includes in its circuit a regulating resistor 41.

The system is evacuated to a low pressure and power is then applied to the transformer 40, so that a glow discharge takes place through the gas between the electrodes 34 and 35 and as a result metal sputters off these electrodes. The plate 11, being directly below the silver electrode 34, is exposed to the sputtering thereof and as a result receives a thin coating of silver on its upper surface. The plate 11 should be located just outside the Crooke's dark space which will appear near the silver electrode 34. The mask 32 prevents the silver from depositing on the edges of the metal plate 11, and making electrical contact therewith to short circuit the finished cell.

It is essential that the temperature of the coated plate be kept low else the selenium will react with the silver and impair the cell. The metal block 31 is provided for this purpose so that it may take up the heat received by the plate 11 during the sputtering process. Heating may also be reduced by keeping the current density low at the electrode 34.

The sputtering is continued until a continuous transparent silver film of the desired thickness is obtained. The gas pressure, current, voltage et cetera should be so adjusted that this will require about 2 to 5 minutes. I preferably use a gas pressure of the order of .01 millimeter of mercury. I have found the following resistance test to give a reliable indication of the condition of the silver.

A pair of test electrodes about  $\frac{1}{2} \times 1$  inch of soft conducting material such as lead foil are affixed to a flat surface being placed side by side with their 1" edges parallel and a space of 2 or 3 hundredths of an inch between them. These electrodes are applied to the silver surface and the resistance between them measured. Anything between 50 and 600 ohms is satisfactory. If the silver has been sputtered on without overheating the cell, a high resistance indicates an insufficient quantity of silver. But if the cell has been overheated so that the thin film of silver has reacted with the selenium to form a selenide, the resistance may be high in spite of the presence of a relatively large quantity of silver.

If the circuit is completed between the terminals of the cell and its sensitive surface is illuminated, a current will flow in the external circuit which varies with the intensity of the illumination. This current is of the order of 100 micro-amperes per lumen on short circuit, and flows by virtue of the inherent action of the cell, no external source of voltage being required. Maximum power output is obtained when the ex-

ternal circuit has a resistance of the order of 1000 ohms.

It will be apparent that the specific embodiment herein shown and described is by way of illustration only. I therefore, do not wish to be limited except by the scope of the appended claims.

I claim:

1. In combination, a plate composed of a metal which reacts slightly with selenium to form a selenide, a layer of selenides on the plate including a selenide of the metal of said plate and a selenide of another metal which metal reacts with selenium to form a selenide more readily than does the metal of said plate, a layer of selenium metal thereover and a conducting layer pervious to light over the selenium metal.

2. In combination, a metal cup, a pair of terminal studs one of which makes an electrical connection with said cup, a metal plate in said cup having a light-sensitive coating on one surface, the other surface of which makes an electrical connection with the other of said studs, insulating means for holding said studs against rotation, for insulating said first stud from said plate, and for insulating said other stud from said cup and a contact member engaging the surface of said coating and said cup to make electrical contact therewith.

3. In combination, a metal cup, a pair of terminal studs one of which makes an electrical connection with said cup, a metal plate in said cup having a light-sensitive coating on one surface, the other surface of which makes an electrical connection with the other of said studs, insulating means for insulating said first stud from said plate and for insulating said other stud from said cup and a contact member engaging the surface of said coating and said cup to make electrical contact therewith, said contact member comprising a beaded portion for engaging said coating and resilient tabs for engaging opposed walls of said cup.

4. In a device of the character described, a base member of the commercial grade of steel known as hot rolled, low carbon mild steel, a layer of selenides of copper and iron thereon, a layer of selenium on the selenide layer and a light permeable conducting layer on the selenium.

5. In a device of the character described, an iron base member, an even surfaced layer of selenide thereon including a selenide of copper and a selenide of iron, a layer of selenium metal on the selenide and a light permeable conducting layer on the selenium.

6. In a device of the character described, an iron base member, an even surfaced layer of selenide thereon including a selenide of lead and a selenide of the iron of said base member, a layer of selenium metal on the selenide and a light permeable conducting layer on the selenium metal.

ANDREW CHRISTY.