Oct. 12, 1937. E. D. WILSON 2,095,781

PHOTOSENSITIVE DEVICE

Filed Jan. 31, 1935

Fig. 1.

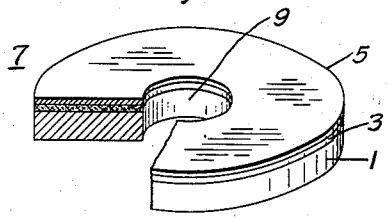


Fig. 2.

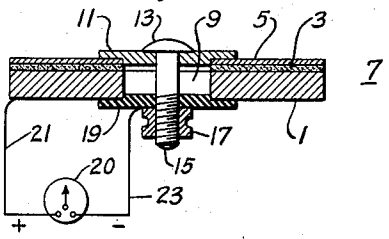


Fig. 3.

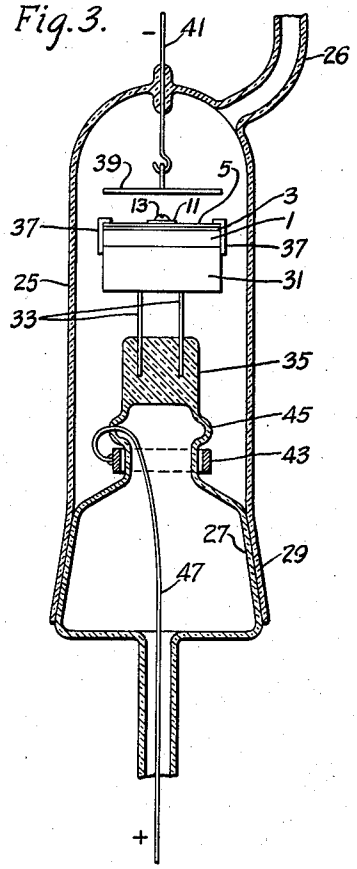


Fig. 4.

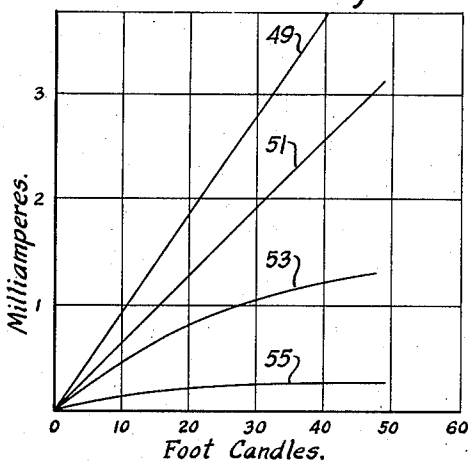
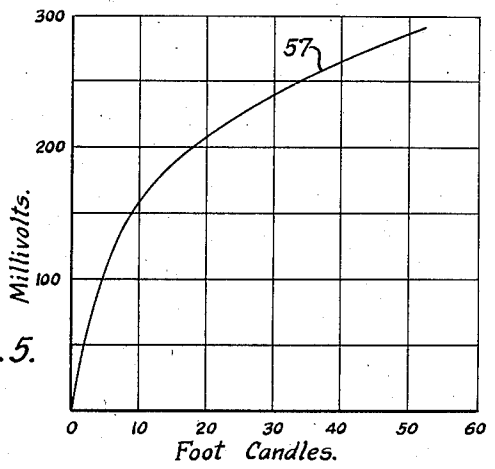


Fig. 5.



WITNESSES:

Leon J. Taza.

R. W. Bailey

INVENTOR

Earl D. Wilson.

BY

F. W. Lysle,

ATTORNEY

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PHOTOSENSITIVE DEVICE

Earl D. Wilson, Wilkinsburg, Pa., assignor to Westinghouse Electric & Manufacturing Company, East Pittsburgh, Pa., a corporation of Pennsylvania

Application January 31, 1935, Serial No. 4,285

2 Claims. (Cl. 136—89)

This application is a continuation in part of my copending application, Serial No. 578,399, filed December 1, 1931 for Photo-sensitive devices.

My invention relates to photo-sensitive devices and has particular relation to photo-sensitive devices of the dry photo-voltaic type.

Photo-voltaic cells constructed and operated according to the teachings of the prior art, of which I am aware, are of several types. One type of cell well known in the art comprises a copper disc having disposed thereon a layer of copper-oxide transparent to ordinary light radiations. Contact is made with the copper oxide through a grid, preferably of spiral structure, that is rigidly clamped against the oxide surface.

In such a cell the photo-electric effect apparently takes place on the inner surface of the copper oxide, that is to say, at the interface between the pure copper surface and the oxide surface. The light is evidently transmitted through the copper oxide and its effect is evidenced by a flow of an electron current from the copper oxide to the copper or a flow of a conventional current from the copper to the copper oxide.

Another type of cell which is well known in the art comprises a solid plate of cuprous oxide which is produced by converting a copper metal plate completely to the oxide by sufficient baking. On one surface of this plate a translucent film of metal is disposed. Contact is made with the film of metal on one surface and with a conducting layer of material sprayed on the other surface of the copper oxide, and when the unit is subjected to the influence of illumination, an electron current flows from the copper oxide to the translucent film of metal.

In experimenting with these cells I have found that the current which flows in the last-named cell between the copper oxide and the translucent film of metal is considerably greater than the current which flows in the first-named type of cell between the copper oxide and the copper. On the other hand, I have found that the copper-oxide disc which, of necessity, must receive rather careful treatment, is an expensive unit, and for this reason is not at all adaptable to the ordinary commercial uses to which the photo-voltaic cell is, at the present time, applied. My experiments also have lead me to the conclusion that, in general, the electron emission excited by light energy in the cells of the photo-voltaic type takes place by reason of some property of the copper oxide and the electrons are emitted by the copper oxide. The direction of emission and its magnitude are probably dependent on the surface in which the light impinges and is absorbed, on the magnitude of the impinging illumination and on the intimacy of the contact between the absorbing surface and its juxtaposed conductor.

It has been the practice in the art to designate the photo-electric effect which is attained when the current flows from the photo-sensitive material to its metallic backing as the "reverse" effect and the effect which is attained when the electron current flows from the photo-sensitive material to the contacting film as the "obverse" effect. Applying these designations to the conclusions of the discussions given hereinabove it appears that, in general, the obverse effect is considerably more marked than the reverse effect.

It is an object of my invention to provide an inexpensive photo-cell of the photo-voltaic type wherein the electron current shall flow away from the metal on which the photo-sensitive material is deposited.

Another object of my invention is to provide a photo-voltaic photo-sensitive element that shall be inexpensive to manufacture on large quantities of the type wherein the emission, arising by reason of impinging radiations, takes place from the surface of the photo-sensitive material facing the source of radiation.

Still another object of my invention is to provide an inexpensive process for preparing a photo-voltaic cell of the type wherein the electron emission takes place from the surface of the material facing the source of radiation that excites the emission.

A further object of my invention is to provide a simple and inexpensive process for preparing a photo-voltaic cell of the obverse type.

More concisely stated, it is an object of my invention to provide an inexpensive photo-voltaic cell that shall yield considerable power as compared with the cells of the prior art and that shall be so inexpensive to manufacture on a commercial scale as to be capable of general commercial applicability.

According to my invention, I provide a cell comprising specifically, a copper plate having deposited thereon a layer of copper oxide. The copper copper-oxide plate is treated in a manner that shall be described hereinafter and after such treatment it is subjected to a discharge in an atmosphere of a highly rarified argon. The discharge takes place preferably between a silver plate and an ordinary electrode and the silver plate is so disposed relative to the copper-oxide surface of the copper copper-oxide plate that a film of silver is sputtered on the surface thereof.

The plate, thus prepared, is provided with suitable elements for contacting the silver film and the copper surface.

I have found that, when such a unit is connected through a suitable meter and is subjected to the influence of light, an electron current flows from the copper oxide to the sputtered silver and is returned through the metal and through the copper to the copper oxide. The current is several times as large as the current of opposite polarity which flows in the cells of the prior art in which the photo-electric effect apparently takes place at the interface of the copper and the copper oxide. On the other hand, the preparation of the unit requires very little in the way of skill in operation or elaborate treatment and is, consequently, considerably less expensive than the pure copper-oxide unit provided in accordance with the teachings of the prior art.

The novel features that I consider characteristic of my invention are set forth with particularity in the appended claims. The invention itself, however, both as to its organization and its method of operation, together with additional objects and advantages thereof, will best be understood from the following description of a specific embodiment when read in connection with the accompanying drawing, in which:

Figure 1 is a view partly in perspective and partly in section, showing an embodiment of my invention;

Fig. 2 is a view partly in section and partly diagrammatic showing a complete cell constructed according to my invention, and provided with the elements necessary for incorporating it in a closed working circuit;

Fig. 3 is a view in section showing a container wherein my cell is treated in the preparation thereof;

Fig. 4 is a graph showing a series of current illumination curves for a cell constructed in accordance with the teachings of my invention; and

Fig. 5 is a graph showing a voltage illumination curve for a cell constructed according to my invention.

The apparatus shown in Fig. 1 comprises a copper plate 1 having a layer of copper oxide 3 deposited thereon. In general, the copper copper-oxide plate 1 may be produced simply by oxidizing one face of an ordinary copper plate. However, it may be of a structure similar to that utilized in ordinary rectifying apparatus and may be produced and treated by the same process as is utilized in the production and treatment of copper copper-oxide rectifiers. As shall be seen hereinafter, it may be of advantage to destroy the rectifying property of the plate, but this object can be accomplished after the plate is produced.

On the surface of the copper oxide a thin film 5 of sputtered metal, preferably silver, is deposited. The film 5 of metal is so thin as to be substantially transparent but for certain applications of my invention, a translucent film is suitable.

The layer 3 of copper oxide on the other hand, should preferably be so opaque as to prevent the transmission of light to the interface and thus to prevent the production of an electron current flowing in a direction opposite to the current for which the plate is particularly provided.

In Fig. 2 a photo-cell constructed according to the teachings of my invention is shown as connected in an electric circuit. The system shown in the view comprises a disc 7 of the type shown in Fig. 1, having an opening 9 therein. Electrical contact is made with the sputtered metallic film 5 on the surface of the copper-oxide layer 3 through a washer 11 which is clamped to the sputtered film 5 by a bolt 13. The bolt 13 passes through the opening 9 in the plate; and its lower threaded surface 15 is engaged by a nut 17 that, in turn, is so tightened as to engage the lower surface of an insulated washer 19. By the clamping action of the nut 17 and bolt 13 the insulated washer 19 is clamped against the copper surface of the photo-sensitive disc 7 while the metallic washer 11 is clamped against the conducting film 5 on the surface 3 of copper oxide.

A lead 21 is soldered to the lower surface of the copper element 1 of the disc 7 while a second lead 23 is firmly secured to the nut 17 that engages the bolt 13. When the device is utilized simply for the measurement of illumination, the circuit through the elements of the disc may be completed through a suitable meter 20. The polarity of the electromotive force set up by the disc under the influence of light is illustrated by the conventional symbols in Fig. 2.

The light passes through the film 5 and strikes the copper oxide surface 3. Electrons are released from the copper oxide surface and travel to the film 5. This electron flow makes the film 5 "negative" according to the accepted current and potential designation and the copper oxide "positive". The electron flow, in the type of device in Fig. 2, is from the film 5, washer 11, bolt 13, lead 23, meter 20, lead 21, copper 1 to the oxide 3.

According to my researches, the photo-sensitive plate 7 may be best provided by suitably treating a copper disc of which one surface has been oxidized. I have found that after the surface is oxidized, the disc should be subjected to several mechanical impulses of considerable magnitude. This object can best be accomplished by depositing the plate on a table placing a wooden block on top of it and hammering the block substantially with an ordinary hammer.

While I am not certain as to the theoretical reasons for the improvement which is attained by hammering the plate, my conjecture is that by such treatment the tendency of the plate to produce an electron current flowing from the copper oxide to the copper base is destroyed. It has been found that hammering destroys the rectifying property of a copper copper-oxide disc, and according to present theories, there is a definite relation between the photo-electric property of a copper copper-oxide disc and its rectifying property.

After having been subjected to the mechanical impulses the plate is alternately dipped into an acid bath and into flowing water until the oxide acquires a glassy cherry red surface. The bath may be preferably concentrated nitric acid. After the plate assumes the proper appearance as described hereinabove, it is thoroughly rinsed and dried, care being taken at the same time, not to deposit any foreign material on its surfaces.

The sputtered film is deposited on the plate in a container 25 equipped with an outlet 26 whereby it may be exhausted. The copper copper-oxide plate is mounted on a stopper 27 provided with a ground surface to engage the ground internal boundary 29 of a conoidal-shaped opening in the container 25.

The copper copper-oxide disc is rigidly secured to a heavy copper block 31 that is, in turn, fastened to a plurality of rods 33 welded in a stem 35 projecting from the stopper 27 for the con-

tainer 25. In practice, it is desirable that the edges of the disc shall not be sputtered and I have provided a suitable mask 37 that is mounted on the copper copper-oxide disc after the latter is secured to the copper block 31. The block 31 is of such size that the copper copper-oxide disc is prevented from becoming hot when subjected to the influence of the sputtering apparatus.

A silver plate 39 is disposed parallel to the copper-oxide surface 3 of the disc and at a short distance therefrom. A lead 41 suitably welded in the walls of the container 25 is connected to the plate 39 and provides a suitable connection to a power supply source (not shown).

The electrode cooperating with the silver plate 39 is preferably a collar 43 suitably mounted on a constricted portion 45 of the stopper 27 provided for the container 25. A lead 47 connected to the collar 43 and welded to the walls of the stopper 27 provides for the connection of the power supply source to the collar.

In the practice of my invention the container 25 is completely exhausted and then filled with argon at a low pressure. My investigations have lead me to the conclusion that for the most desirable results the container 25 must be first evacuated as completely as possible. The pressure of the argon should be from .4 to .5 millimeters of mercury. This pressure may be measured if desirable with an ordinary gage. However, I have found that for all practical purposes the pressure may be suitably estimated by noting the character of the discharge through the gas.

After the container has been completely exhausted and suitably filled with the rarified argon, the collar 43 is then connected to the positive terminal of an approximately 750 volt power source while the silver plate 39 is connected to the negative terminal thereof. A discharge is thus produced in the container and is continued for fifteen seconds, after which it is found when the disc is removed from the block 31, that a thin layer 5 of silver has become sputtered on the surface 3 of the copper oxide.

In Figs. 4 and 5 graphs are shown giving the general characteristics of a photo-cell constructed according to my invention. In Fig. 4 the current transmitted by a cell in milliamperes is plotted as ordinate, while the light flux impinging on the cell in foot candles is plotted as abscissa.

As will be noted in Fig. 4, a family of curves 49, 51, 53 and 55 is plotted. The parameter for the curves is the resistance connected in the circuit with the cell 7. The four resistances utilized in taking the curves 49, 51, 53 and 55 shown in the view were respectively 1 ohm, 11 ohms, 100 ohms and 1000 ohms.

In Fig. 5, the voltage output of a cell constructed according to my invention in milli-volts is plotted as ordinate and the light flux impinging on the cell in foot candles is plotted as abscissa. The curve 57 shows the characteristic of an average cell.

In discussing the features of my invention I have referred hereinabove, in general, to a photo-cell of the copper copper-oxide type. While my invention is specifically applicable to a cell of this type, a number of the features discussed herein are equally as well applicable to photo-voltaic cells of other types, such, for example, as the cell made up of an iron plate, a selenide deposited on the plate and a silver deposit on the selenide layer. To the extent to which my invention applies to cells of other types, it is understood that the applications of my invention to such cells are equivalents which lie within the scope thereof.

Again while discussing the elements of my invention, I have referred, in general, to silver as the preferable contacting material to be utilized with the copper copper-oxide disc. While I have found that silver yields highly satisfactory results, it is possible that other metals may exist which would yield as satisfactory results, or which would be applicable for cells utilized for a particular purpose. These other metals are, particularly, gold and platinum that form with silver the group of noble metals that have a very high conductivity even in the thin substantially transparent film as described in connection with my photo-electric devices. These metals add the desired photo-electric effect in combination with the copper oxide, and yet withstand undesirable chemical action and, accordingly, protect the photo-sensitive device, in addition to their photo-electric effect. If gold is used, this gold has the advantage that it readily passes the green portion of the spectrum to which the human eye is most sensitive and, accordingly, a cell with the gold layer as the photo-active material in combination with the copper oxide, will have a color sensitivity comparable with that of the human eye. My invention is, therefore, not to be restricted to a cell incorporating only a silver contacting surface.

Although I have shown and described certain specific embodiments of my invention, I am fully aware that many modifications thereof are possible. My invention, therefore, is not to be restricted except insofar as is necessitated by the prior art and by the spirit of the appended claims.

I claim as my invention:

1. As an article of manufacture, a photo-sensitive device comprising an opaque copper plate, an opaque layer of copper oxide formed on at least one surface thereof and a translucent layer of metal in intimate contact with said layer of copper oxide.

2. As an article of manufacture, a photo-sensitive device comprising opaque copper having an opaque layer of copper oxide on at least a portion of the surface thereof and a translucent metallic layer on said layer of copper oxide.

EARL D. WILSON.