

# The Manufacture of Photo-Electric Cells

By J. BERTHILLIER. (From *Électricité*, Vol. 31, No. 126, April, 1947, pp. 69-74, 13 illustrations.)

THE photo-electric cells considered in this article are of the photo-emissive type and should be clearly distinguished from photo-voltaic or photo-conductive cells which are not directly based on the electron principle. Since the first experiments by Becquerel, photo-emissive cells have been considerably improved, both as regards sensitivity and current output.

Overall sensitivity has been increased by using cesium instead of the alkali or alkaline earth metal layers originally employed (in the earliest types of cells, hydrided magnesium, obtained by passing a glow discharge through hydrogen gas, and later hydrided sodium or potassium were used). Spectral sensitivity has been improved by endeavoring to obtain maximum response to the light sources most generally used for excitation, i.e., tungsten filament lamps with a radiation rich in red and infra-red rays, and ordinary daylight, with a greater blue radiation component. Two types of cathodes have been specially developed for these two sources, viz.: the cesium-oxide and the antimony cathodes, and their production will be described in this article. The spectral sensitivity curves of these two cells are

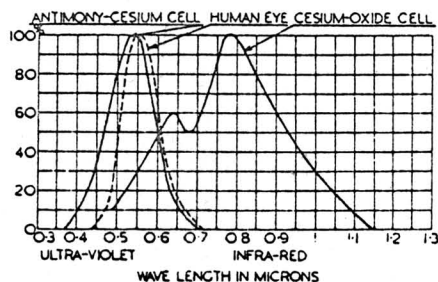


Fig. 1.

shown in Fig. 1, the current output being indicated not as an absolute value but as a percentage relative to the corresponding wavelength of the incident light.

## CESIUM OXIDE CATHODES.

The cesium-oxide layers are generally much more complex than the formula ( $\text{AgCs}_2\text{O}$ ) by which they are characterized. Experiments with cesium metal deposited on a silver plate and then subjected to gradual oxidation did not give successful results. It was thus necessary to use a substratum of silver oxide to support the superficial film of cesium, the various layers diffusing into each other at a molecular scale so as to form a complex surface (Fig. 2). Cesium oxidizes immediately in the presence of air and therefore cesium metal films can only be examined in vacuum or in an inert gas such as argon. The general method for preparing these layers is to get metallic cesium to react at a determined temperature with a layer of silver oxide previously prepared.

The cathode is of silver or of electrolytic copper covered with an electrolytic deposit of silver. The materials employed must be very nearly pure, even more than in the case of wireless valves, as the slightest traces of certain elements can reduce the photo-electric properties or be the cause of defective functioning. The cathode is generally designed as a cylindrical plate in order to have a potential gradient as homogeneous as possible over the entire cathode surface. The anode is a straight rod usually of nickel, situated at the center of the cylinder, all the photo-electrons thus being subjected to the same attractive force.

Each of the two electrodes is connected through a

vacuum-seal passage to two external conductors which are subsequently fixed on to the socket. The base contains, as usual in all bulbs, a press, i.e., a small tube used for pumping (see Fig. 3). The glass used for the bulb must be free from lead salts, but the base is generally of lead glass, for reasons which will be explained later. To maintain intimate contact these two types of glass must have nearly the same thermal expansion coefficients over a fairly large temperature range.

**Pumping.** The cells are first evacuated in the same way as ordinary light bulbs, that is, a good vacuum of about  $10^{-5}$  mm mercury must be reached, the bulb then being baked at about 400 deg. C. to eliminate residual gases and the water vapor adhering to the walls.

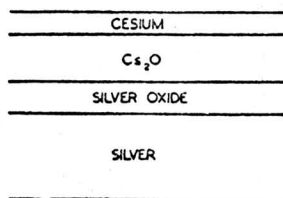


Fig. 2.

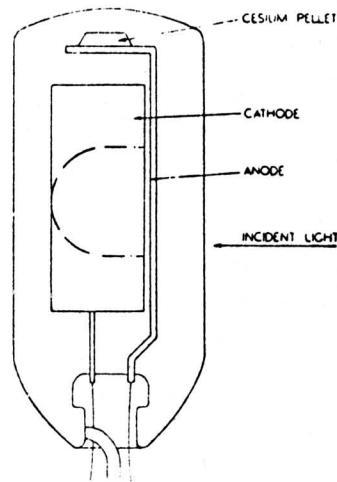
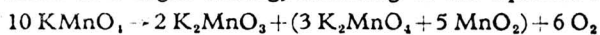


Fig. 3.

Induction heating of the cathode metal is not possible because of the tendency of silver to evaporate at 600 deg. C. which would then result in a coloring of the walls and an absorption of light. Therefore a particularly thorough outgassing before assembly is required.

**Oxidation.** After baking and cooling, extremely pure oxygen at a pressure of about 1 mm is admitted into the cell. This is achieved, for instance, by decomposition of purified potassium permanganate as a result of a slight heating, according to the equation:



A superficial oxidation of the silver is obtained, for instance, by means of a current discharge (preferably d.c.) between the cathode and the anode, using a potential of about 500-600 volts, with an output of a few milliamperes. The extent of the oxidation can be regulated either by varying the oxygen pressure, i.e. calculating the fixed quantity of oxygen for a given weight of silver, particularly in the case of very thin films on glass (semi-transparent cathodes), or more generally by observing the color acquired by the silver. The oxide layer determines by interference with light a series of characteristic colors which depend on the film thickness and not on the condition of the surface, the cycle of colors being, in the order of increasing oxide thicknesses: yellow, orange, violet, blue, green, yellow, red, green, etc. The blue color corresponding to a thickness of about 800 molecules of oxide is generally chosen as giving the best results.

**Preparation of cesium.** The cesium which has to be made to react with the silver oxide is extremely oxidizable, and should therefore be prepared only just

before using, either in the cell itself, or in an adjacent container, under vacuum. Various reactions can be employed, such as the reduction of a cesium salt (chloride, dichromate, chromate, etc.) by a reducing metal (zirconium, silicon, aluminum, etc.); and one of the most generally used reactions is



The reaction occurs at a temperature of 700-800 deg. C. To obtain this reaction, a pellet consisting of a compressed pulverized mixture of cesium salts and reducing metal (with an excess quantity of the latter, to facilitate a complete reaction) is inclosed in a metal cup, which is then heated by means of eddy currents induced by a high-frequency generator. The cesium thus liberated deposits on the walls of the ampoule containing the cup in the form of a slightly yellowish metal which is liquid at temperatures above 28 deg. C. and which can, therefore, be ejected by a slight heating of the wall by contact with a hot surface.

*Activation.* Three processes can be applied for the final preparation of the layer. The first consists in producing just the quantity of cesium required to obtain a suitable layer. This quantity can be calculated roughly for a given amount of silver oxide and then be more accurately determined after a few tests. In this case the cesium is prepared in the cell itself and the cup is placed as indicated in Fig. 3. The entire cell is then heated to about 200 deg. C. The cesium is ejected from the cup and deposits on the cathode which has remained comparatively cold. When the cathode reaches a temperature of 180-190 deg. C. the reduction of the silver oxide by the cesium will take place.

In spite of its simplicity, this method is not frequently used, as the optimum composition of the sensitive layer must be very accurately determined, a slight excess or lack of cesium leading to a much lower sensitivity. As there are two slightly variable constants in this process (the quantity of oxide which depends on a determination of color or of pressure, and the amount of cesium which can vary within certain limits, according as the reaction is more or less complete), a certain amount of error is involved. For instance, the reaction depends on the size of the grains of powder and the homogeneity of the mixture. Furthermore, a third factor which can have a considerable effect is the absorption of cesium by other parts such as the anode, the glass, etc., or, on the contrary, the liberation of oxygen fixed by these surfaces during the oxidation.

The second process, developed from the first, consists in preparing slightly more cesium than theoretically necessary and having it absorbed in excess of the required amount. The glass base of the bulb can also have a part in this process. When cesium is heated in the presence of lead glass, it will reduce the lead oxide of the glass, so that lead metal will be liberated, this being evidenced by a blackening of this glass. The excess cesium can thus be eliminated by the lead glass in the press or base, but lead glass should not be used in the bulb, to avoid producing an opaque surface. A similar reaction can also be obtained with an easily reducible oxide (copper or lead oxides) deposited at any convenient position in the cell.

The cesium can be ejected on to the cathode in the same way as in the first activation process. The cell is gradually heated while the base is subjected to an adjustable amount of additional heating, so that a certain equilibrium is obtained between the reaction on the cathode and the absorption of the excess cesium by the base. This process requires considerable skill and a good knowledge of the variation of colors of the layers, and is not therefore suitable for industrial work.

The third process is the easiest to apply: the cesium is produced in an adjacent container and introduced gradually into the cell through a calibrated capillary tube.

In this manner just the right quantity is admitted, and the cesium reservoir is then cooled so that it will retain the excess metal. A lead glass base can also be used to absorb the excess cesium, and a particularly good arrangement is to introduce the cesium through the lead glass press. Although some of the cesium is absorbed while passing through it, the reaction is sufficiently slow to let a certain amount pass through to the cathode. As the reaction with the lead oxide only begins at 140 deg. C. and becomes more and more rapid with increasing temperatures, this method enables a nearly automatic regulation of the amount of cesium to be achieved.

*Regulation of the activation.* The problem is to determine the moment at which the cathode reaches its maximum sensitivity. The first suggestion would be to reproduce operating conditions, that is, to illuminate the cathode with a constant light source, and to apply a d.c. voltage between the cathode and the anode, and follow the rise of the current flowing through the circuit. There is, however, a disturbing factor: the thermionic emission of the cesium oxide is much greater than the photo-electric emission at the reaction temperature of 180-200 deg. C., and as, furthermore, the thermionic current varies considerably with temperature, its fluctuations are of the same order of magnitude as the photo-electric current.

There are, however, two accurate methods of determining the activation of the cathode. The first is to measure the thermionic current in order to find its maximum, as in the case of normal layers this also corresponds to maximum sensitivity.

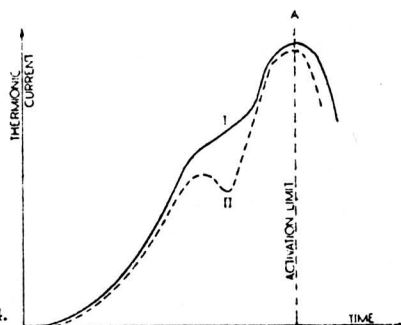


Fig 4.

Consider for instance a cell for which the cesium has been prepared in an adjacent appendage. The two units are heated in an oven up to a given temperature between 180 and 200 deg. C. (the temperature variation not exceeding  $\pm 2$  deg.). The two electrodes of the cell are connected to a d.c. supply and a microammeter is included in the circuit. The variation of current against time will then be observed to follow a course such as that of curve I in Fig. 4. As soon as the maximum current is reached (point of inflexion A) the cell and its appendage are both rapidly removed from the oven. The thermionic current will then drop rapidly, while at the same time the photo-electric current (which can be measured by another method still to be described) will rise considerably because of the external illumination if the point thus determined is the actual maximum of the current. It should be noted that sometimes curves such as curve II have been recorded, with a secondary maximum corresponding to an unstable condition of the layer. If the cell is removed at this moment, the thermionic current will drop rapidly but no photo-electric current will be registered.

Conditions may vary slightly according to the structure of the cell. For instance, in a cell with a massive cathode within the bulb, part of the free cesium may condense on the walls which cool more rapidly after the cell has been taken out of the oven. In such a

## ANTIMONY-CESIUM CATHODES.

These cathodes have a response curve which is displaced relative to that of the cesium-oxide type cells, and the processes for their preparation are also different. The layers are merely an alloy of antimony and cesium, which need not be prepared in exact proportions, but the activation temperature is a function of the relative quantities of cesium and antimony used.

The antimony is generally deposited as a very thin layer by evaporation under vacuum at about 300 deg. C., and various methods can be employed.

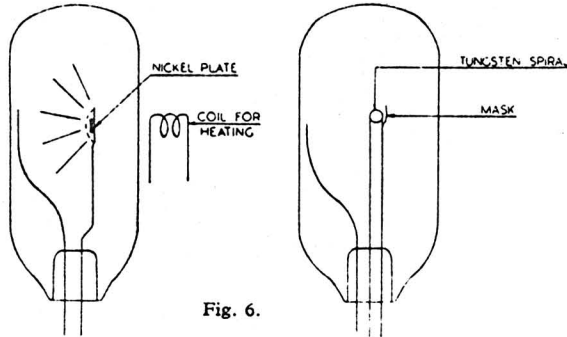


Fig. 6.

The piece of antimony metal can for instance be placed on a nickel plate on the top of the anode and held in place by a thin wire meshing (Fig. 6). On heating with induced currents the metal molecules are projected towards the rear, while the front surface of the bulb is kept free for the incident light. A wire contacting with the glass cathode is then connected to the cathode terminal. Certain authors point out that cathodes prepared in this way do not give optimum response, the evaporated metal containing a certain proportion of nickel. Furthermore, the plate holding the antimony must be large enough to enable it to be heated without using an extremely powerful generator, but a plate of this size is then an obstruction to light and reduces the useful area. For these reasons a tungsten spiral covered with an electrolytic deposit of antimony is sometimes used instead of the previous arrangement.

Once this layer has been obtained, the cesium vapor can either be made to react at a fixed temperature according to determined proportions, or cesium can be introduced even without heating, the temperature of the assembly being then raised to a value depending on the amount of cesium employed.

A characteristic feature of these processes is the more or less total absence of thermionic currents, probably because no oxygen is available to react with the cesium. The activation can thus be followed by simple photoelectric measurement. For the case of a gradual admission of cesium at constant temperature, the sensitivity curve as a function of time is shown in Fig. 7. The first plateau which may sometimes even have a slight depression seems to correspond with a first alloy formation which is relatively stable but with a sensitivity well below that of the real maximum.

The arrangements for the admission of cesium do not differ for these cathodes from those employed for cesium-oxide cathodes which have already been described. However, because of the type of alloy used, their preparation is much easier. Whereas in the case of silver-oxide base-layers an excess of cesium results in a definite loss of sensitivity, due apparently to a complete reduction of the intermediate layer of silver oxide which cannot be reversed, with antimony-cesium cells, if there is an excess of cesium and a corresponding lack of sensitivity relative to the optimum value, this can be eliminated by absorption according to the methods already described.

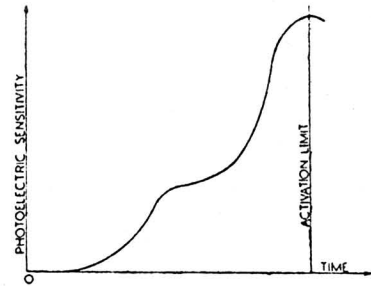


Fig. 7.

**Response.** Few articles have been published on the superactivation of these cells. Under normal conditions a mean sensitivity of 15-20 microamperes per lumen can be expected with an incandescent lamp light at 2,700 deg. K., which is a much lower value than that for the cesium-oxide cathodes; but the sensitivity peak is in the blue region, which means that with another source such as daylight this sensitivity will be much higher. Therefore, for the electronic equipment using such radiations (for instance, scanning equipment, daylight regulated cells, etc.) these layers will be far superior to the  $\text{AgCs}_2\text{O}$  type layers. It does not seem that these cells have been produced with a gas

filling, and this may restrict their possibilities. A great advantage is the excellent electrical conductivity of very thin layers, which are therefore very transparent to light, whereas this is not the case with cells with a silver substratum.

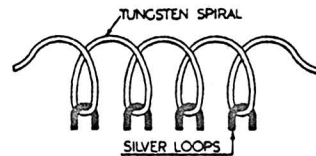


Fig. 8.

Silver has good evaporating properties. Evaporation can be achieved for instance by fitting little silver loops on to a tungsten wire which is then heated up to 1,200-1,500 deg. C. (Fig. 8). Extremely thin layers can thus be obtained on the cathode and their thickness can be determined from their opacity to light. But a limit to the fineness of the layers is given by the so-called mosaic phenomenon. When heated in the presence of air or under vacuum the layer changes gradually into a discontinuous structure, under the influence of surface tension, and at higher temperatures the silver forms into minute spheres varying from 1 to 20 microns in size which adhere firmly to the supporting surface. The discontinuous surface has a very high resistivity and the potential of the different parts of the cathode is not sufficiently determined, since the grains emitting negative electrons then acquire positive potentials. This phenomenon also tends to occur during oxidation in the pre-treatment of the cathode or when the silver film is in contact with air after evaporation. Antimony does not have this drawback, and can therefore be used to make thin films with a transparency as high as 80 per cent. Antimony-cesium cathodes give greater current outputs than the cesium-oxide cathodes without fatigue, and the saturation limit is less definite in antimony-cesium cells (see Fig. 9).

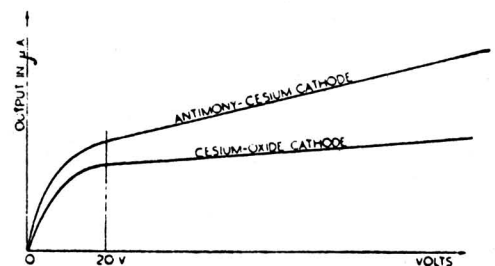


Fig. 9.