

The Alkali Metal Photoelectric Cell

By HERBERT E. IVES

INTRODUCTION

IN the development of the commercial system of picture transmission now in operation over certain of the Bell System lines, one of the initial problems was the choice of a method of transforming the light and shade of the picture to be transmitted into properties of an electric current. There are in general two methods of accomplishing this. The first, which we may term the photo-mechanical method, utilizes some photographic process to produce a mechanical structure, which may be used either to make and break contact, or to produce mechanical movement of some element whose motion produces a variable electric current. The second method consists in the utilization of some light sensitive device which produces or varies an electric current.

An indispensable requirement in the electrical transmission of pictures is *speed* in conveying the picture from one point to another. The choice of a method of transforming light and shade into an electrical current will therefore, other things being equal, be that method which requires the least time for the transformation. It is on this basis that the photo-mechanical methods were not favorably considered in this development. The preparation of the line or dot structure image, similar to the half tone plate, or the preparation of a photo-relief, are processes which cannot be completed in less than one to two hours, and involve a delay which in many cases would seriously detract from the advantages of electrical transmission over other means now available, such as the airplane.

In choosing a photo-sensitive device for this purpose, certain requirements had to be met. The light responsive device should be as nearly as possible instantaneous in its action. The response should also be proportional to the light intensity. These requirements cannot be met by any photo-sensitive devices of the group whose resistance changes under the action of light, such as selenium. The field was therefore limited to the *photoelectric cell*, of the type in which the effect of light is to release electrons from the surface of the light sensitive element and so cause an electric current to flow in the space between the light sensitive surface and another electrode. Photoelectric cells are considerably less sensitive than the best variable photo-resistances, but while this characteristic would have made them difficult to utilize in the earlier days of efforts at picture transmission, the development of vacuum tube amplifiers admirably fitted for amplifying photo-

electric currents has remedied this deficiency. A further requirement, that the light sensitive device should preferably be sensitive to visible radiation, ruled out the use of those sensitive materials sensitive chiefly to infra-red or ultra-violet radiation. All of these requirements pointed to the *alkali metal photoelectric cell* as developed by the work of Elster and Geitel and others.

GENERAL CHARACTERISTICS OF PHOTOELECTRIC CELLS

The typical photoelectric cell consists of a hermetically sealed glass bulb containing an atmosphere of gas at a low pressure, and provided with two electrodes, one of which is the light sensitive material. In the schematic cell shown in Figure 1, *K* is the photo-sensitive material

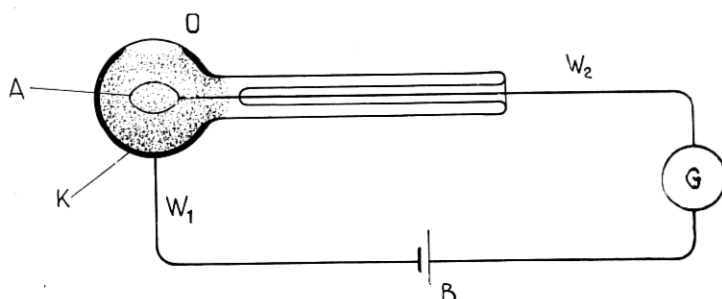


Fig. 1—Schematic central anode photoelectric cell.

(cathode), for instance an alkali metal such as potassium, which is spread upon the inside wall of the glass bulb and is connected with the exterior of the bulb by a sealed-in wire, w_1 , *A* is the other electrode (anode). As here shown, it is a simple metallic ring connected with a second wire, w_2 , carried through the stem of the bulb. The two electrodes are shown connected together through a battery, *B*, and galvanometer, *G*. The operation of the cell consists in letting light fall upon the cathode through the window, *O*. The resulting current may then be measured by the galvanometer, or utilized to operate suitable apparatus.

A complete study of the photoelectric cell resolves itself into obtaining knowledge of the effect of varying a number of factors which enter into its construction and use. Of these we may note: the material which is used for the light sensitive surface, and the treatment to which this material is subjected; the composition and pressure of the gaseous atmosphere; the shape and disposition of the various elements, that is, the *structure* of the cell. We must investigate the relationship

between the quality of the light falling upon the cell and the electric current produced. We must in addition consider certain other physical variables which must be met with in practice, notably temperature.

CHARACTERISTICS OF CELLS OF VARIOUS STRUCTURES

For purposes of discussion we may classify photoelectric cells in regard to structure as *central cathode cells* and *central anode cells*. As the terms imply, these two extreme types of cells differ in the position of the photoelectric material. The central anode type of cell is shown in Figure 1. The sensitive material entirely covers the walls, so that the cathode is of relatively large area. The central cathode cell is illustrated in Figure 2, in which the symbols are the same as in Figure 1.

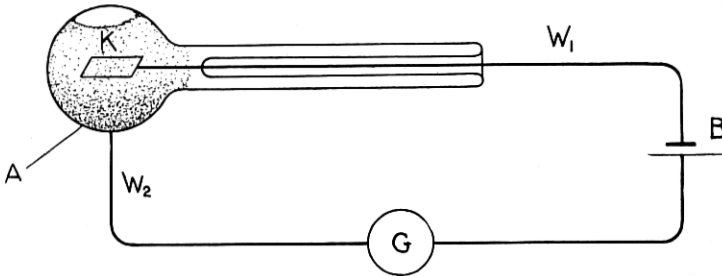


Fig. 2—Schematic central cathode photoelectric cell.

In this the walls of the cell are covered with a non-light sensitive material (e.g. silver), and the sensitive material is coated upon a relatively small centrally placed electrode.

CENTRAL CATHODE CELLS

Central cathode cells possess certain decided advantages for the theoretical study of photoelectric phenomena and have consequently been used in many of the more important photoelectric investigations. The simplest case to consider first is that of the high vacuum cell, that is one containing no appreciable amount of gaseous atmosphere. When a constant light is incident on the light sensitive cathode, and a series of voltages are applied to the terminals of the cell, voltage-current relationships are obtained of the character shown by any one of the curves of Figure 3. Several significant points are to be noted about these characteristic curves. We find that the photoelectric current starts at a definite positive value of the voltage. This voltage is called the "stopping potential." It varies with the wave length of the

exciting light. This is shown in the figure by the several curves for different wave lengths, varying from λ_1 , representing short wave energy, such as blue light, to λ_3 , long wave energy such as yellow. The shorter the wave length (the higher the frequency), of the exciting light, the higher must be the positive potential necessary to prevent or stop the emission of electrodes under illumination. As the positive potential is reduced, the photoelectric current increases, until the applied field (or the effective field if contact potential differences are present) becomes zero. At this point, the current becomes *saturated*, that is increase of voltage in the negative direction fails to increase the current. This means that the applied field does not penetrate to any appreciable depth into the photoelectric material.

Characteristic curves of the type shown in Figure 3, have played a

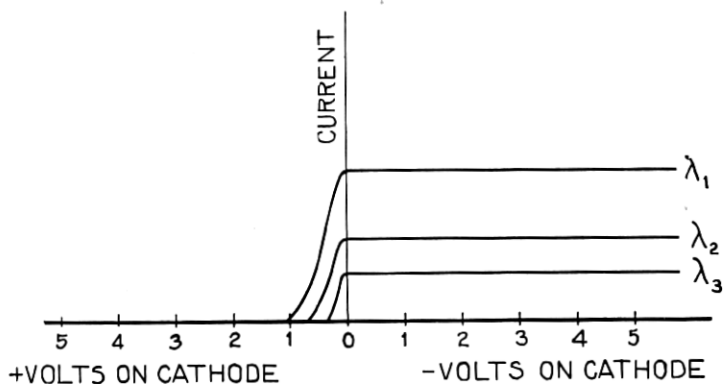


Fig. 3—Voltage-current curves for typical central cathode vacuum photoelectric cell.

very important part in the development of photoelectric theory, and particularly of the quantum theory. If V is the voltage applied to the cell, e the charge on an electron, h the quantum constant, ν the frequency of the exciting light, Einstein predicted and Millikan has shown experimentally that the following relationship holds: $eV = h(\nu - \nu_0)$, where ν_0 is the limiting frequency corresponding to the long wave length limit, beyond which the photoelectric emission does not occur. If m is the mass of the electron, and v its velocity, the above relation can be written $\frac{1}{2} m v^2$ (Velocity²) = $h(\nu - \nu_0)$. From this expression it is evident that the greater the interval between the frequency of the light used, and the limiting frequency, the higher is the velocity of emission of the photoelectrons.

When instead of being highly exhausted, the cell has an atmosphere of gas at a low pressure (a few tenths of a millimeter of mercury) the

condition of saturation typical of the high vacuum cell for high negative voltages no longer holds. Instead the photoelectric current is increased by the occurrence of ionization, by collision of the electrons initially produced with the molecules of gas. The current increases with applied voltage in the manner shown in Figure 4, until at some value characteristic of the kind of gas in the cells, the gas breaks down and a visible electrical discharge takes place. The amplifying effect of the gaseous atmosphere increases with the pressure of the gas up

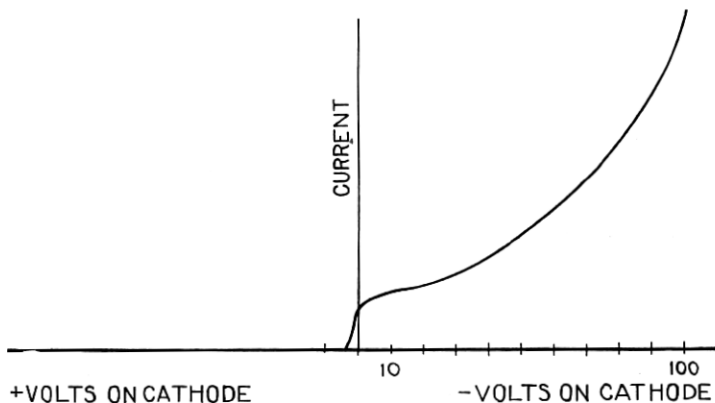


Fig. 4—Voltage-current curves for typical central cathode gas filled photoelectric cell.

to a maximum and then decreases. The value of this optimum pressure depends on the kind of gas and the dimensions of the tube. The best pressure is usually a few tenths of a millimeter of mercury.

As the illumination of the cell is changed, the current changes in exact proportion, that is the illumination-current relationship is rectilinear. This relationship holds for both the vacuum and gas cells provided there are no free glass surfaces on which charges may accumulate. If the window is made too large it may become charged and cause an appreciable curvature of the illumination-current relationship.

CENTRAL ANODE CELLS

In cells with a relatively small centrally placed anode, the voltage-current relationship differs from that of the central cathode cells most noticeably in that high applied voltages are necessary in order to insure saturation. Typical voltage current curves for short (λ_1) and long (λ_2) wave length energy, for a central anode cell consisting of a

spherical anode and concentric spherical cathode are shown in Figure 5. The rate at which saturation is approached with voltage varies with the wave length of the exciting light. The longer the wave length, the slower the electrons, as shown above, and the more quickly are they captured by the central anode.

When gas is introduced into a central anode cell, we again have ionization by collision, and the voltage-current curve is turned upward

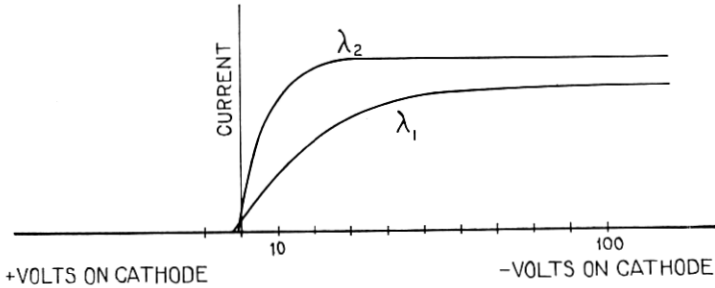


Fig. 5—Voltage-current curves for typical central anode vacuum cell.

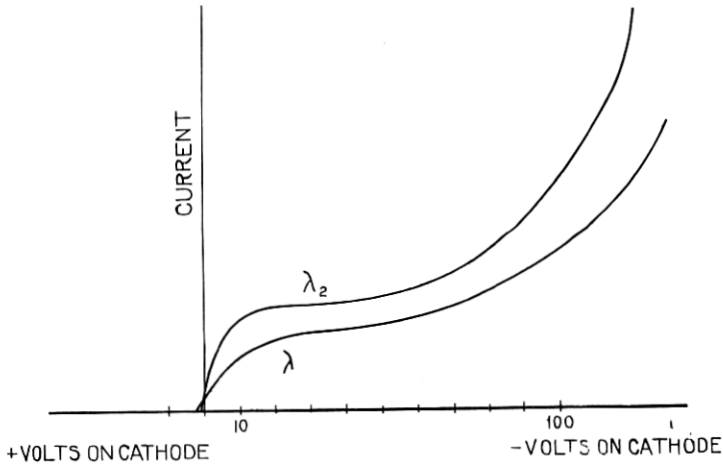


Fig. 6—Voltage-current curves for typical central anode gas filled cell.

from the voltage axis in the manner shown in Figure 6. As in the case of the central cathode cells, the current increases with voltage until the critical potential for the gas is reached.

The illumination-current relationship is rectilinear in the central anode cells, as it was in the central cathode cells, provided the precautions as to avoiding free glass surfaces, already mentioned, are observed.

INFLUENCE OF THE NATURE OF THE IRRADIATION

The magnitude of the photoelectric current depends upon the angle of incidence, the plane of polarization and the color or wave length of the light used. This dependence is closely interlinked with the choice of the photo-sensitive material and the state of its surface. For the purpose of separating out the effects of the several variables in the incident light, it is necessary to study the properties of optically plane or specular surfaces of the photo-sensitive material. Such surfaces can only be obtained with the alkali metals by raising them above their melting points, by forming alloys, or by depositing extremely thin films on a polished underlying metal surface such as platinum. Specular surfaces of the alkali metals obtained in these several different ways exhibit differences in their behavior, but it will be sufficient for the present purposes to disregard these secondary differences and to speak merely of the photoelectric current from specular surfaces when the incident light varies in wave length in certain typical ways, or is polarized.

INFLUENCE OF THE PLANE OF POLARIZATION

When light is incident at a steep angle on a specular surface, the two extreme conditions of polarization are those in which the electric vector lies in the plane of incidence and that in which it lies perpendicular to the plane of incidence. In the first case, the electric vector has a component perpendicular to the surface. In the latter case the electric vector lies parallel to the surface. It has long been known that the amount of light absorbed by a metal surface is, in general, greater when the electric vector is in the plane of incidence. Consequently, since photoelectric emission must be due primarily to the absorption of the energy from the incident light, it is to be expected that the photoelectric current will be greater for light polarized with the electric vector in the plane of polarization. Such is actually the case, but while the ratio of absorption of light, for the two planes of polarization, at say 60° incidence, never rises above a value of four for any of the alkali metals, the ratio of the photoelectric currents under the same conditions may mount to a very high value, such as 20 or 30 to one. This effect is particularly noticeable in the liquid alloy of sodium and potassium, and in the case of all the four alkali metals, sodium, potassium, rubidium and caesium, when these spontaneously deposit in a high vacuum upon a polished surface. It is very much less marked in the case of the pure alkali metals in the molten condition. Typical examples of the influence of the plane of polarization

on the photoelectric effect are shown in Figure 7, where the symbol \parallel indicates that the electric vector is in the plane of incidence, the symbol \perp that it is perpendicular to this plane.

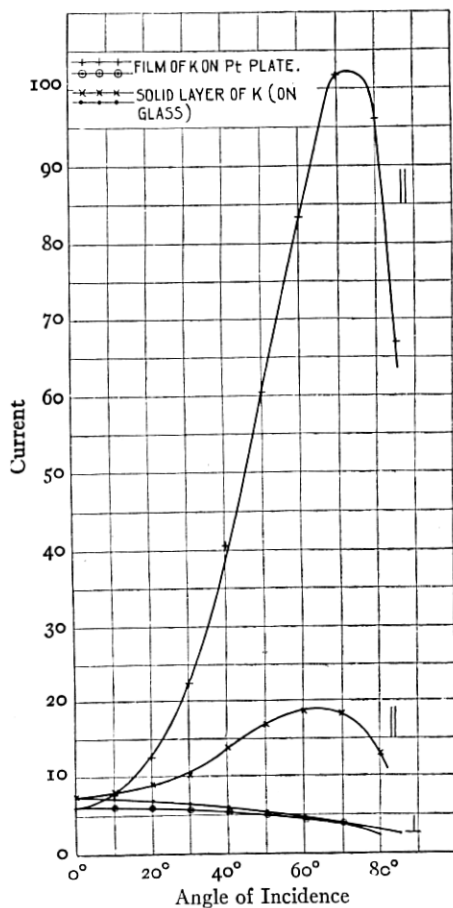


Fig. 7—Photoelectric emission from a specular surface of solid potassium, and from a thinly coated platinum plate, at various angles of incidence; electric vector in plane of incidence (\parallel); electric vector perpendicular to the plane of incidence (\perp).

DISTRIBUTION OF RESPONSE ACCORDING TO WAVE LENGTH

When the exciting light is incident either perpendicularly on a specular alkali metal surface, or at a high angle of incidence with the plane of polarization such that the electric vector is parallel to the surface, the response for equal intensities of monochromatic radiation

through the spectrum is as shown by the curve marked \perp in Figure 8. Photoelectric emission is entirely absent on the long wave side of a certain wave length which is known as the *long wave length limit*. From this wave length, the emission rises gradually and uniformly toward the short wave or blue end of the spectrum.

When the incident light is polarized so that the electric vector has a component perpendicular to the surface, the wave length distribution of response follows the general character shown in the curve marked \parallel in Figure 8. Correlating the wave length distribution of response with

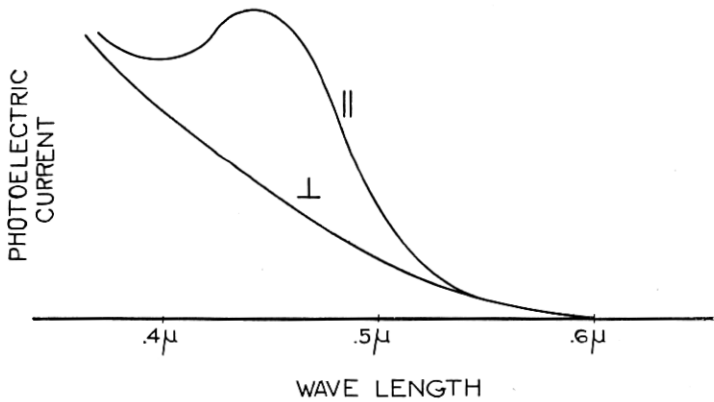


Fig. 8—Wave-length distribution of response from specular alkali metal surface; electric vector in plane of incidence (\parallel); electric vector perpendicular to plane of incidence (\perp).

the variation of emission with the plane of polarization considered in the last section, the general conclusion may be drawn that the enhanced emission for light with the electric vector in the plane of incidence is due largely to radiation falling within a narrow spectral region. The magnitude of this wave length peak varies greatly with different materials. The maximum occurs at a wave length different not only for the different alkali metals, but also for different modes of securing the specular surface. This wave length maximum has the appearance of being due to some resonance phenomenon, and its variation in position through the spectrum according to the method of preparation of the surface is connected in some unknown way with the state of binding of the alkali metal atom on the surface with the body of material beneath.

THE PHOTOELECTRIC CURRENT FROM ROUGH SURFACES

With rough surfaces of alkali metal, the plane of polarization of the incident light no longer has meaning. We would therefore expect no

significant difference in the total emission from a really rough surface when the plane of polarization of the incident light is changed; and such in fact is the case. We would also expect that the distribution of response according to wave length would be a mixture of the effects of the two planes of polarization. This also is found to be so. Rough surfaces show the wave length maximum characteristic of light polar-

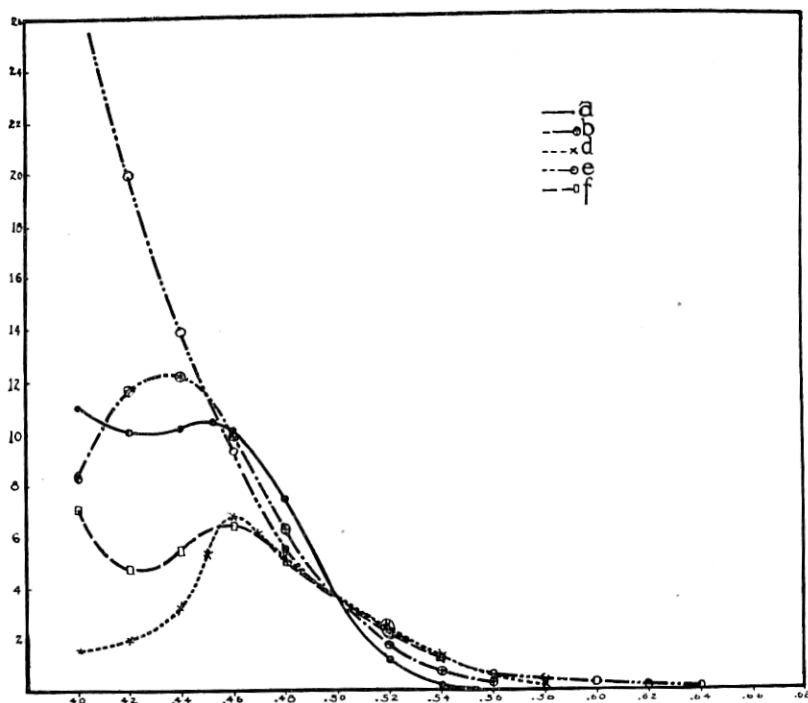


Fig. 9—Wave-length distribution of emission from rough surface potassium photoelectric cells, showing variation from cell to cell depending on difference of treatment.

ized with the electric vector in the plane of incidence on a specular surface. Depending on the degree of roughness and the method of preparation of the surface, the wave length maximum is different in size and also in position. In Figure 9 are shown several wave length distribution curves for potassium cells in which the surface is roughened and colored by a hydrogen glow discharge. These cells differ both in respect to their absolute sensitiveness, in the position of their maximum sensitiveness, and the extent of their sensitiveness toward the red end of the spectrum. It has not as yet been found possible to prepare photoelectric cells with properties uniform from one cell to another.

INFLUENCE OF THE PHOTOELECTRIC MATERIAL
AND ITS TREATMENT

The alkali metals differ in their photoelectric sensitiveness in a perfectly definite order, which is that of their degree of electro-positiveness, as shown by their position in the periodic table of the elements. The variation in sensitiveness is correlated with the extension of sensitiveness in the spectrum. This progresses regularly from sodium, which in its pure state is not photoelectrically sensitive beyond about $.58\mu$, through potassium and rubidium, to caesium, which is photoelectrically sensitive in the near infra-red. The exact terminations of sensitiveness in the spectrum depend upon the character of the surface and its treatment, and have not been exactly correlated with any other properties of the material.

In order to attain the greatest sensitiveness with the alkali metals, these are commonly subjected, in the preparation of the photoelectric cell, to what is called the *coloring* process, discovered by Elster and Geitel. This consists in subjecting the surface to a glow discharge in an atmosphere of hydrogen. The result is to color the otherwise silvery alkali metal a rather deep blue-purple or blue-green. The exact cause of this color is not known, but it has every appearance of being due to the production of small (colloidal) particles of alkali metal. The greater sensitiveness is probably due to the increased effective surface presented by the colloidal particles rather than the increased absorption coefficient of the darker color. Similar colors may be obtained by distilling the alkali metal in a very thin layer on glass and the color of the surface changes when observed by polarized light in much the same manner as do colloidal surfaces of other sorts.

After the completion of the coloring process, it is necessary to remove all the hydrogen from the cell by pumping. Otherwise the surface will revert to its original uncolored form. In order to obtain the amplifying effect of a gaseous atmosphere, it is customary to introduce an inert gas, such as argon or helium, into the cell.

Cells made in the manner just outlined are reasonably permanent in their important characteristics. Elster and Geitel have made potassium cells in this manner, which when connected with a delicate electrometer exhibited a degree of sensitiveness approximately that of the human eye. According to what has gone before, the most sensitive cells should be obtained if rubidium or caesium are used in place of potassium. It is found however by experiment that rubidium, and particularly caesium, do not lend themselves so well to the coloring

process, probably because of their lower melting points, and hence cells made of potassium may represent practically the best performance which is now attainable.

EFFECT OF TEMPERATURE

It has long been held that the photoelectric effect is independent of temperature. Recent experiments, however, have shown that the alkali metals are affected in their photoelectric response by variation of temperature. A typical set of data for potassium is shown in Figure 10. It will be noted that the influence of temperature is small

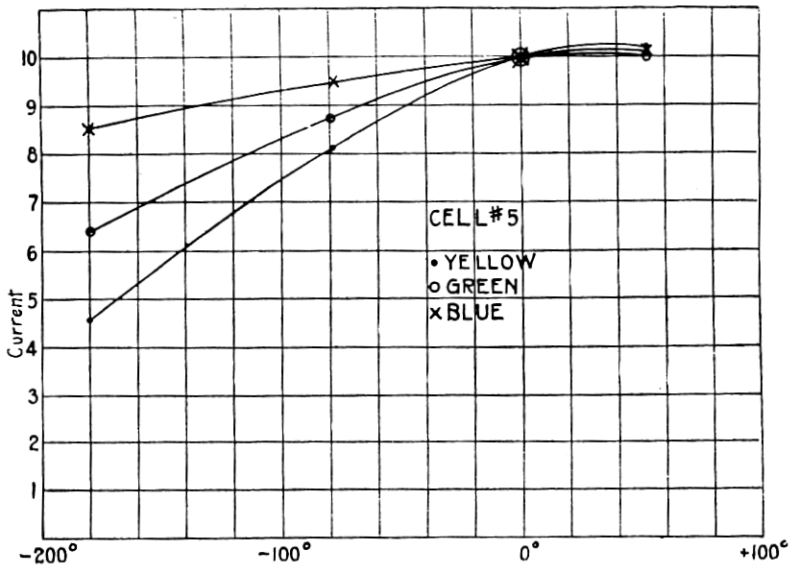


Fig. 10—Variation of photoelectric sensitiveness of potassium with temperature.

for the shorter wave lengths of light, but considerable for long wave excitation. These data were secured in highly exhausted cells of pure alkali metal. When gas is present or a large amount of alkali metal vapor can deposit on the cooled surface, the effect of decreased temperature may be to increase the photoelectric current. It will be noted that the changes shown in Figure 10 are insignificant over the ordinates range of room temperatures, and for practical purposes, particularly for picture transmission, the effects of temperature on the performance of photoelectric cells may be taken as negligible.

PRACTICAL FEATURES OF CELLS AS USED

The photoelectric cells as used for picture transmission are classified, according to the above discussion, as central anode, gas filled, colored cells. The shape of the cells is that shown in Figure 1, and also in the photograph, Figure 11, with which is an accompanying scale. The cells are made of pyrex glass, which is chosen because it is highly resistant to corrosion by potassium during the distillation stages. The very long neck of the cells is dictated partly by the space into which the cells are placed in the picture transmission apparatus, in

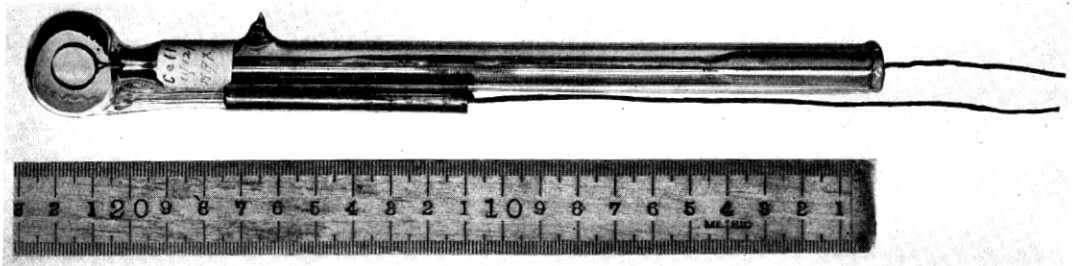


Fig. 11—Photograph of photoelectric cell of type used in picture transmission.

part by the desirability of having as long an insulating space as possible. Where, as in earlier types of photoelectric cells, the alkali metal is in close proximity to the other electrode, leakage currents over the glass surface greatly interfere with accurate results. (In working with extremely small currents it is desirable to have in addition to the considerable length of glass insulating path, a metallic guard ring in the stem of the cell, which may be earthed.)

The alkali metal ordinarily used is potassium. This is introduced by distillation on the pump. The cell is first baked to a temperature of 400° C. for several hours while on the pump in order to drive out all traces of water vapor. The potassium for use in making up the photoelectric cells is first of all distilled in a vacuum into long glass tubes. In this preliminary distillation, the greater part of the absorbed gaseous impurities are removed. After the cell has been baked out on the pump, a piece of the glass tube containing potassium is broken off and introduced into the pump system. Between the point of introduction and the cell are a series of bulbs. The potassium after melting in vacuo is distilled successively through these bulbs and into the photoelectric cell, where it is condensed on the walls of the bulb. A window is then made in the cell by applying a small flame on the appropriate

part. The next step is to introduce a small amount of pure hydrogen gas, which is permitted to enter from a reservoir on the system. This hydrogen gas goes through the system of bulbs through which the potassium has been distilled, which still contain a large amount of potassium, and is thereby cleaned of all traces of gases or vapors which might react on the potassium in the cell. A glow discharge is then

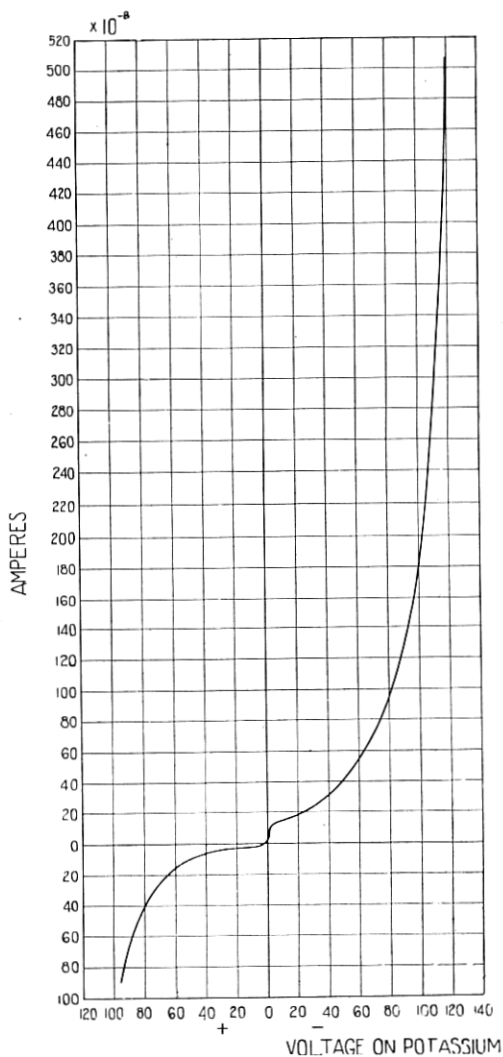


Fig. 12—Typical voltage current characteristic of potassium photoelectric cell as used in picture transmission. Incident luminous flux = .015 lumen.

passed from a high voltage source, until, by illuminating the alkali metal surface and reading the current on a sensitive galvanometer, it is found that a maximum of sensitiveness has been attained. The hydrogen is then completely removed by long continued pumping. The final step in the preparation of the cell consists in the introduction of a small quantity of carefully purified argon. The argon for this purpose is held in a reservoir in which there is a pool of sodium-potassium alloy. By passing an electric discharge from this pool to an electrode through the gas, the argon is purified of all active impurities. It is introduced into the cell through the same series of potassium coated bulbs already mentioned, the potassium in the meantime having been vigorously heated to drive off all occluded hydrogen, so that the gas when it finally reaches the photoelectric cell is entirely inert. The gas pressure is carefully adjusted while the cell is still on the pump so as to give an optimum effect, after which the cell is sealed off.

Typical voltage-current characteristics of the cells thus made are as shown on Figure 12, where the currents indicated are those obtained from an illumination of 100 meter candles from a vacuum tungsten lamp, the aperture of the cell being 1.5 sq. cm. It will be noted that, unlike the ideal characteristic shown in Figure 6, the actual cells shows a small current in the opposite direction for positive voltages applied to the sensitive surface. This is because practically it is very difficult to prevent some alkali metal from depositing on the anode, which thus becomes light sensitive, and responds to the scattered and reflected light in the cell.

For use in the picture transmission apparatus, the cells are mounted in tubular metal cases, from which they are insulated by hard rubber rings attached to the glass stem, by sealing wax. The cells in their cases are handled as units; and are sufficiently rugged to be readily shipped from place to place. Their characteristics remain practically unchanged indefinitely.

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