

Jan. 28, 1936.

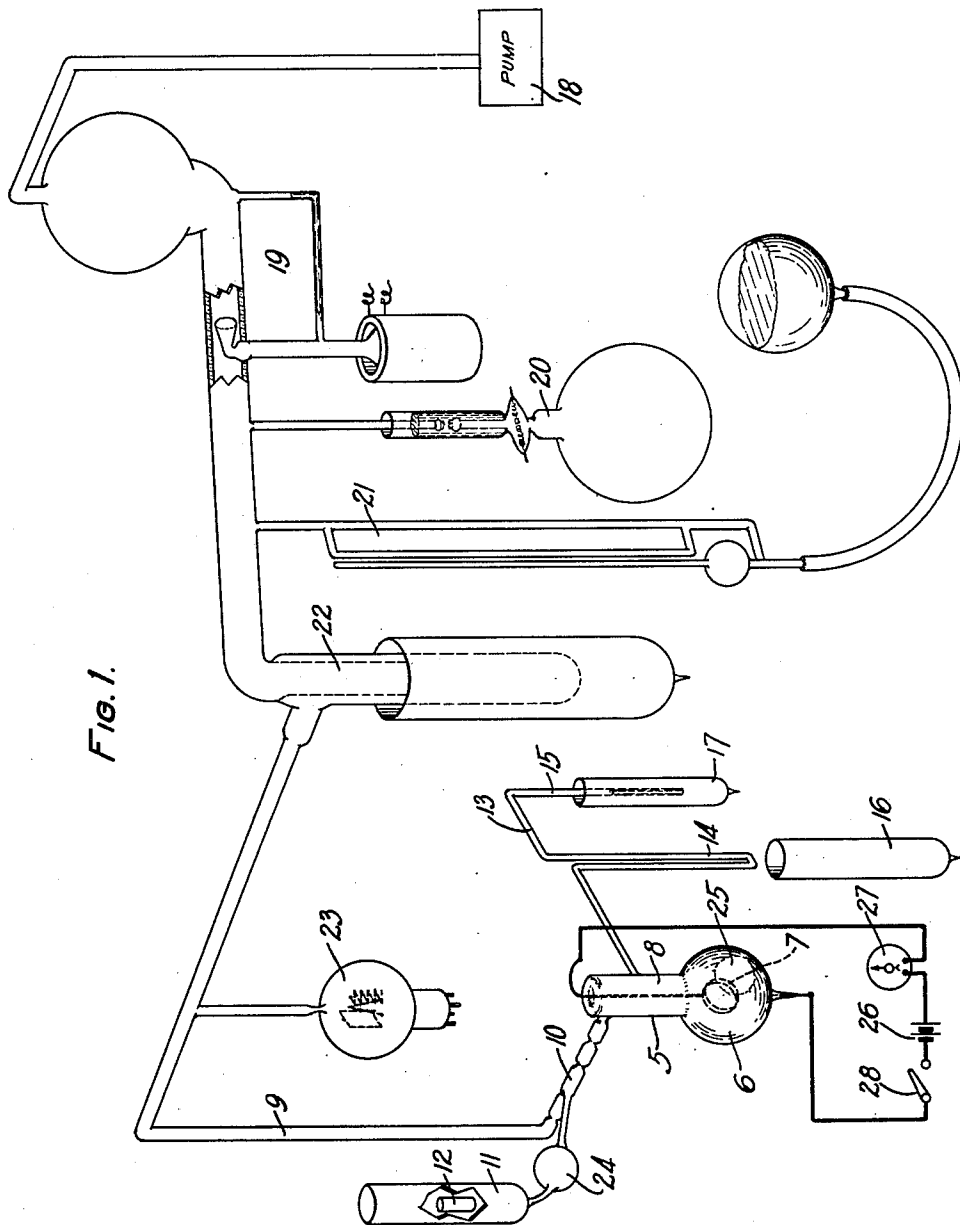
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2,029,040

PHOTO-ELECTRIC TUBE

Filed April 18, 1929

4 Sheets-Sheet 1



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4 Sheets-Sheet 2

FIG. 2

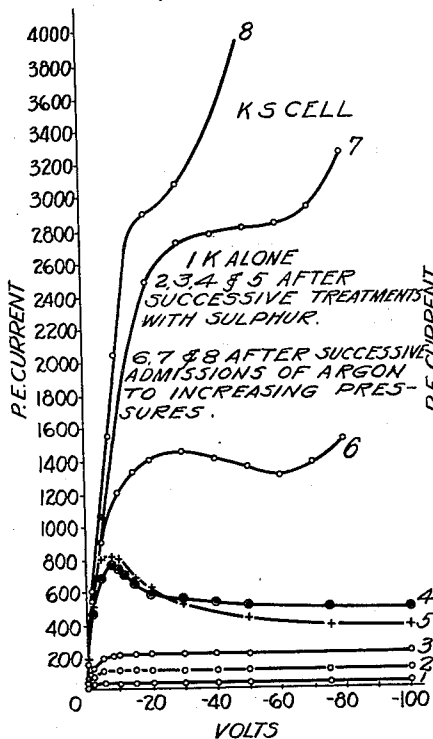


FIG. 3

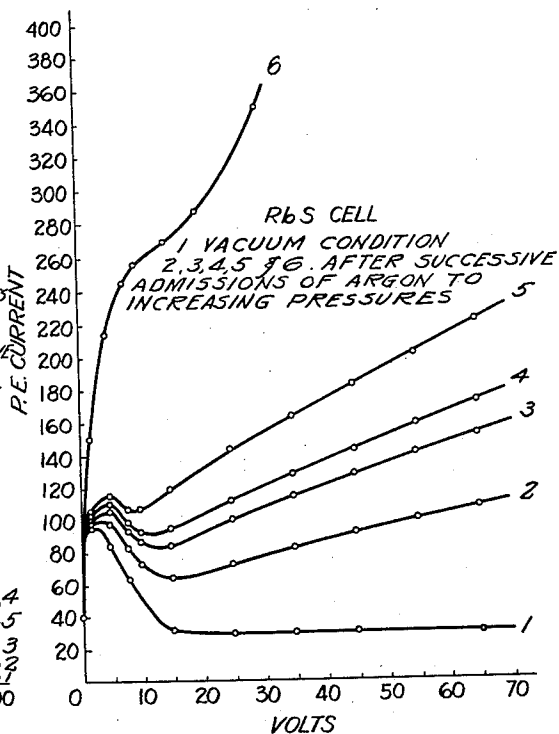


FIG. 4

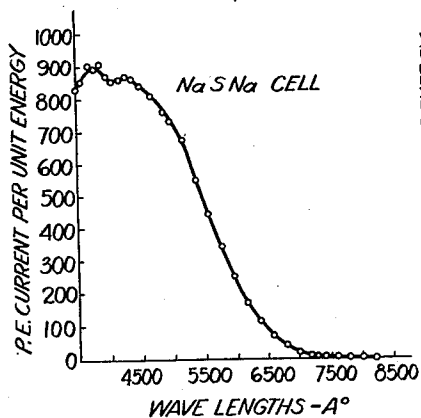
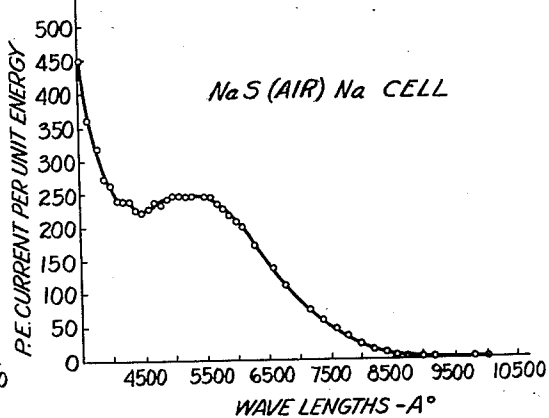


FIG. 5



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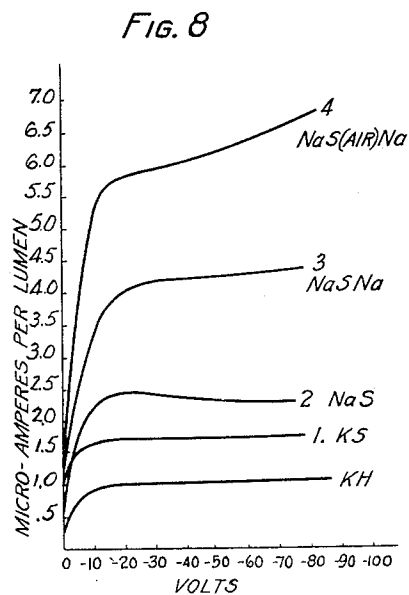
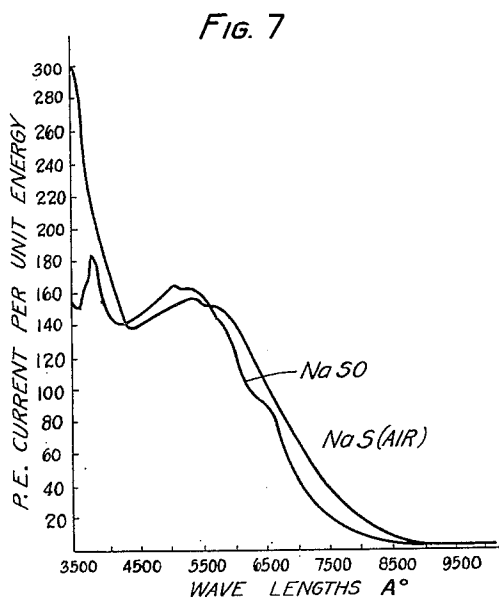
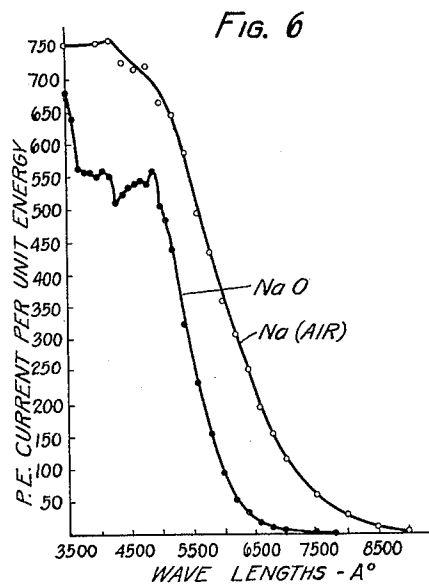
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PHOTO-ELECTRIC TUBE

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4 Sheets-Sheet 3



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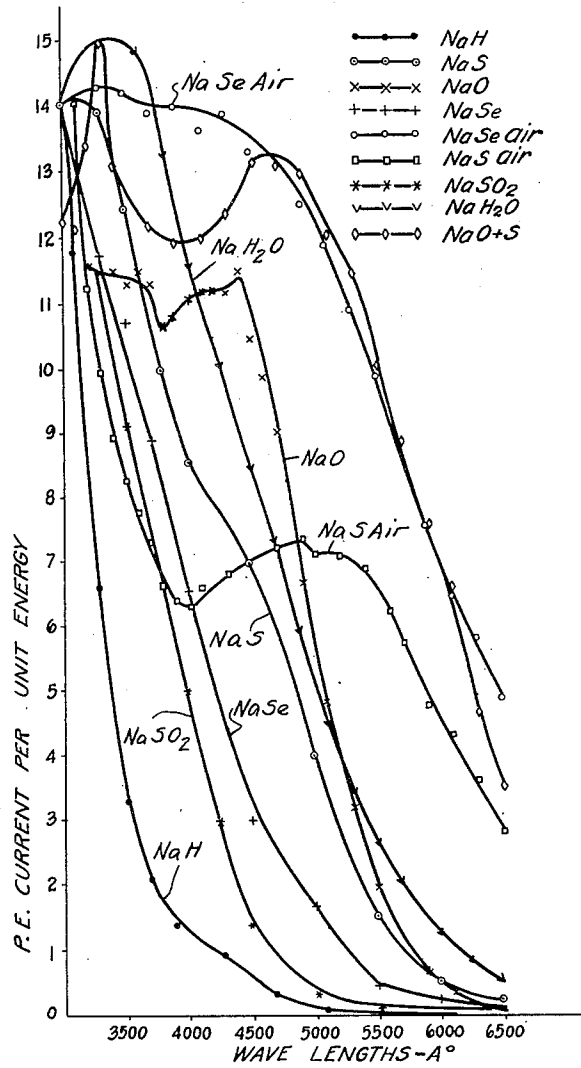
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4 Sheets-Sheet 4

FIG. 9



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PHOTO-ELECTRIC TUBE

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Application April 18, 1929, Serial No. 356,095

14 Claims. (Cl. 250—27.5)

This invention relates to light-sensitive electric devices and methods of making them.

An object of the invention is to increase the sensitivity of photoelectric tubes.

5 The current variations generated by photoelectric tubes are so small that for most purposes they have to be very greatly amplified. In accordance with the present invention photoelectric tubes having greatly increased sensitivity are provided. The invention in certain aspects is in the nature of improvements upon photoelectric tubes in which a layer of dielectric material is associated with the photoelectric material to increase or to modify the sensitivity, as for example, by increasing sensitivity to red light, and upon the methods of making such tubes. Tubes of this type are described in a patent of A. R. Olpin, No. 2,008,874, patented July 23, 1935, on application Serial No. 353,176, filed April 6, 1929, in which the present invention is also described at some length. The two inventions were the outgrowth of researches directed to the improvement of photoelectric tubes. As stated at length in the Olpin application, the use of the dielectric in association with the photoelectric material may greatly increase the sensitivity and may be made to bring up the sensitivity for desired wave length regions; the effect apparently being due at least in part to the ability of the dielectric material to modulate incident light, for instance red light, with a resonance frequency of its own to produce light of different wave length which in turn acts upon the photoelectric material. In accordance with certain aspects of the present invention the sensitivity of tubes employing a dielectric in association with the photoelectric material is increased by placing some of the photoelectric material upon the dielectric material in the form of a very thin layer. This appears to increase the effectiveness of the dielectric.

Another feature of the invention is an improvement in photoelectric tubes brought about by admitting atmospheric air or other gas containing moisture to the tube during its manufacture after photoelectric material has been deposited therein, reevacuating and again depositing photoelectric material, preferably in the form of a very thin layer.

Another feature of the invention is the method of making a photoelectric tube containing layers of photoelectric material and dielectric intimately associated which comprises determining when the proper amounts of the materials have been deposited by noting the photoelectric current while deposition is taking place and stopping

deposition when the sensitivity reaches a definite value.

Other features and objects of the invention will appear from the following description and the appended claims.

A more detailed description of the invention will now be given having reference to the accompanying drawings.

Fig. 1 shows schematically a layout of the apparatus used in making photoelectric tubes according to this invention.

Figs. 2 to 9 are curves showing characteristics of tubes made up according to this invention.

Referring to Fig. 1, the apparatus used in making photoelectric tubes according to this invention will now be described. The tube proper comprises a glass vessel 5 having a substantially spherical-shaped portion 6 which is about two inches in diameter. The cathode of the tube is formed on the inner surface of the portion 6. An anode 7 in the form of a nickel ring is supported from the stem 8. The tube 5 is connected to a vacuum pump station by a glass tube 9. Between the tube 9 and the tube 5 is a distilling tube 10 to which is connected a side tube 11 within which photoelectric material within a glass capsule 12 is placed prior to being distilled into the tube 5. A tubulation 13 comprising a U-shaped portion 14 and a sealed end-tube 15 is also sealed to the stem 8 of tube 5 through which the various dielectric materials employed according to this invention are introduced. Dewar flasks 16 and 17 are provided for cooling the U-tube 14 and the dielectric tube 15, respectively.

The vacuum pump station comprises a vacuum pump 18, a mercury vapor pump 19, an arrangement 20 for introducing inert gas, a McLeod pressure gauge 21, a liquid air trap 22 and an ionization gauge 23.

The method of making a tube in which the photoelectric material is sodium will first be described by way of example. The cathode of the tube comprises an opaque layer of sodium, the surface of which is treated with the gaseous material evolved from flowers of sulphur when heated, a thin film of sodium then being formed on the resulting surface. Preparatory to the formation of the opaque layer of sodium a capsule 12 of previously purified sodium is inserted in the chamber 11 which is then sealed. Likewise flowers of sulphur are placed in the tube 15 which is sealed to the tubulation 13. Prior, however, to the formation of the opaque layer the system is thoroughly evacuated and the tube 5 outgassed by heating. The chamber 11 and the capsule 12

are then heated until the sodium within the capsule 12 is sufficiently molten to break through the end crust of oxide and flow into the bulb 24. The chamber 11 is then sealed off from the bulb 24.

5 From the bulb 24 the sodium is successively distilled through the bulbs of the distilling tube 10 to form an opaque layer of sodium on the inside of the spherical member 6. By means of a point flame a window 25 about one inch in diameter is

10 made on one side of the bulb 6 through which to introduce the exciting light. After the sodium coating has been formed the side tube 15 is heated until the sulphur melts. During the time that the sulphur is being heated, a test circuit

15 comprising battery 26 and galvanometer 27 is completed by the closing of switch 28 in order that any change in response to light may be noted readily. The pump is left running during the treatment of the surface. The sulphur sublimes

20 easily with little additional heating, so that it is easy to control the amount entering the photoelectric tube 5. Light from a constant source is directed normally through the window onto the back of the tube. The amount of dielectric introduced is determined by the sensitivity conditions desired.

It has been found that the sensitivity of the tubes can be increased by introducing enough dielectric in the manner just described to reduce the sensitivity to a steady value and then introducing

30 a thin film of sodium thereon. This thin film is best obtained by applying a point flame to heat the material around the edge of the window 25. The response of the tube to light under this condition is about double that when the surface is in its most sensitive condition without the film of sodium. The increase in sensitivity is chiefly in the red and infra-red regions as shown in Fig. 4.

Another step in improving the sensitivity is the

40 introduction of an additional thin layer of dielectric obtained by again heating the flowers of sulphur in the tube 15 or by warming the U-tube 14, if this tube had been cooled previously during the heating of the sulphur. The amount of dielectric here admitted is preferably just sufficient to produce maximum sensitivity.

At this stage in the development of red sensitive sodium tubes an accident was capitalized to produce a surface having the greatest response to

50 light of any previously studied. This improved photoelectric tube was especially sensitive to long wave light, the greatly enhanced selective maximum in the spectral distribution curve broadening appreciably and the long wave limit shifting out to at least 1 μ , as shown in Fig. 5. The

55 accident referred to was the cracking of a tube leading to an almost completely made tube, letting in air at atmospheric pressure. The crack was repaired and the tube reevacuated.

60 No photoelectric emission whatsoever was obtainable from the surface in that condition, but when a thin film of sodium was deposited on this surface the result was an exceptionally sensitive tube. Moreover, that the resulting tube was not

65 a freak has been proved by the making of many other tubes into which air was deliberately admitted.

It appeared that the effect of air on the surface was to cause a broadening of the new selective

70 maximum on the long wave side or possibly a shift of this maximum toward the red. Fig. 6 shows that pure Na surfaces can be sensitized to long wave-lengths by air and oxygen alone, but comparison with Figs. 5 and 7 indicates the advantage of the presence of sulphur vapor. In

comparing the spectral distribution curves of different figures the significant characteristic is the shape of the curves rather than the absolute values of the ordinates. For a comparison of the relative sensitivities of various types of tubes reference may be had to Fig. 8.

In Fig. 8 is given the relative electron yield for a typical potassium hydride tube, a potassium tube treated with sulphur vapor, a sodium tube similarly treated, another such sodium tube with

10 a thin film of sodium deposited on top of the dielectric and finally a sodium tube treated with both sulphur vapor and air as described above. The emissions are in terms of microamperes per lumen, and the color temperature of the exciting

15 light is 2848° K.

The stability of the tubes was apparent when a constant light was left incident on the cathode surface for over an hour without so much as one-half of one per cent change in current out-

20 put.

The same procedure as that described in connection with sodium tubes, may be followed in the making of photoelectric tubes in which the photoelectric material is potassium. Other alkali

25 metals may also be used for the photoelectric material, the technique of forming the base layer being modified as necessitated by the nature of the material used. Other dielectric materials may of course be used.

Caesium has been used as the photoelectric material, a thin film of caesium being formed on a caesium hydride surface. Such a tube shows the sensitivity to red light characteristic of the other tubes made according to this invention previously

35 described herein. In the making of such a caesium tube a thin film of caesium on magnesium may be first flashed in hydrogen, after which another thin film of caesium is formed on the resulting surface.

The response to various intensities of light was checked for both potassium and sodium surfaces sensitized by the methods described above over an extended range and found to be linear. The variations in light intensity were effected by

45 moving the lamp source along a photometer track. The measurements were made on a Compton electrometer, using the steady deflection method.

The words "sulphur vapor" have been used

50 advisedly in the foregoing description, for it was early discovered that the actual sublimation of sulphur onto the surface was not essential. In fact, equally good tubes were made with only the volatile gases liberated from sulphur on heating.

55 These gases could be held in the liquid air trap 14 between the sulphur tube 15 and the tube 5, and then by lowering the liquid air flask properly, the amount of gas actually entering the coated tube could be accurately determined.

A surprising observation was the very slight amount of gas actually necessary to produce the most sensitive tubes. Both the oil and mercury vapor pumps are left connected to the tube and running throughout the sensitizing process and the pressure of the gas on the surface is seldom higher than that to be found in most so-called

65 "good vacua". An amount scarcely detectable with an ionization manometer gauge is effective in changing the emission immediately upon its entering the tube. The amount of gas actually occluded or contained in commercial flowers of sulphur is very small. A large number of photoelectric tubes have been made according to this

75

invention. The spectral distribution curves for some of these are shown in Fig. 9.

Once the dielectric film begins to build up, as shown by a change in the surface color, the current values are larger at low voltages than at high. This has been quite generally observed with this type tube, the voltage current curves showing a maximum sometimes at cathode voltages as low as -5 volts. When argon is admitted at low pressures, however, the gas curves increase from this maximum. A typical series of these voltage-current curves for a potassium surface treated with sulphur vapor is shown in Fig. 2. Since the irregularities they exhibit could be ironed out by focussing the light on the side of the tube, or by shining it through a ground glass, they appeared to be due to directional effects caused by the geometry of the tube.

The voltage vs. current curve shown in Fig. 3 is unique in that the current reaches its maximum value with not more than minus three volts on the cathode rapidly decreasing to a constant value from about minus twenty volts up. The admission of argon at low pressure into the tube, however, shows an amplified effect at voltages less than the ionization potential of the gas as was also the case with potassium tubes.

Throughout this application the convention has been followed, in symbolically indicating the nature of a cathode, of using the chemical symbols for designating the materials used, the symbol for the base layer of photoelectric material appearing first.

The curves shown in the accompanying drawings may or may not be truly representative of the properties of that particular type of tube at its best, but they represent the properties of the tube when made according to the best technique known at the time the data was obtained.

The term "light" as herein used is intended to cover not only light within the range of the so-called visible spectrum but also electromagnetic radiations both above and below that range.

By the term "equi-energy" curve is meant a curve wherein the ordinate refers to photoelectric emission per unit of incident light of a particular wave length. In the accompanying drawings the curves plotted between wave length and photoelectric current per unit of impressed energy are equi-energy curves.

The term "alkali metals" as herein used is intended to include the alkaline earth metals.

The symbol $\text{\AA}$ represents angstrom units of wave length.

The term "atmospheric air" signifies the normal air of the atmosphere or other gases having the constituents usually found in the atmosphere, an important one, besides nitrogen and oxygen, being water vapor.

What is claimed is:

1. A photoelectric tube including an anode and a light sensitive electrode having a base metallic layer, a thin layer of dielectric thereon, a thin film of light sensitive material on said dielectric, and another thin layer of dielectric material upon said thin film of light sensitive material.

2. A photoelectric tube including an anode and a light sensitive electrode having a base layer of sodium, a thin layer of dielectric material thereon, and a thin film of light sensitive material on said dielectric material.

3. A photoelectric tube including an anode and a light sensitive electrode having a base layer of sodium, a thin layer of dielectric material thereon, a thin film of sodium on said dielectric mate-

rial, and another thin layer of dielectric material upon said thin film of sodium.

4. A photoelectric tube including an anode and a light sensitive electrode having a base metallic layer, a thin layer of sulphurous material thereon, a thin film of light sensitive material on said sulphurous material, and another thin layer of sulphurous material upon said thin film of light sensitive material.

5. A photoelectric tube including an anode and a light sensitive electrode having a base layer of sodium, a thin layer of sulphurous material thereon, and a thin film of sodium on said sulphurous material.

6. The method of making a photoelectric tube comprising an evacuated vessel having electrodes including a light sensitive conductive electrode element therein, which comprises impressing a voltage upon said electrodes insufficient to produce a glow discharge, depositing a layer of dielectric material of increasing thickness upon said element, noting from time to time the photoelectric current, increasing the thickness of said dielectric material until an added increment does not produce any further change in the photoelectric current, and depositing a layer of photoelectric material upon said dielectric material until the photoelectric current reaches a steady value.

7. The method of making a photoelectric tube comprising an evacuated vessel having electrodes including a light sensitive conductive electrode element therein, which comprises impressing a voltage upon said electrodes insufficient to produce a glow discharge, depositing a layer of dielectric material of increasing thickness upon said element, noting from time to time the photoelectric current, increasing the thickness of said dielectric material until an added increment does not produce any further change in the photoelectric current, depositing a layer of photoelectric material upon said dielectric material until the photoelectric current reaches a steady value, and depositing the dielectric material upon said photoelectric material until further increase of photoelectric current ceases.

8. The method of making a photoelectric tube comprising an evacuated vessel having electrodes including a conductive electrode element therein which comprises producing an opaque layer of sodium upon the inner walls of said vessel in contact with said element with a light transmitting window therein, impressing a voltage upon said electrodes insufficient to produce a glow discharge, depositing a layer of dielectric material of increasing thickness upon said layer of sodium, noting from time to time the photoelectric current, increasing the thickness of said dielectric material until an added increment does not produce any further change in the photoelectric current, heating the vessel with a point flame near the edge of said window until the photoelectric current reaches a substantially steady value, and again depositing dielectric material until further increase of photoelectric current ceases.

9. The method of making a photoelectric tube comprising an evacuated vessel having electrodes including a conductive electrode element therein which comprises producing an opaque layer of sodium upon the inner walls of said vessel in contact with said element with a light transmitting window therein, impressing a voltage upon said electrodes insufficient to produce a glow discharge, depositing a layer of dielectric material of increasing thickness upon said layer of sodium, 75

- noting from time to time the photoelectric current, increasing the thickness of said dielectric material until an added increment does not produce any further change in the photoelectric current, heating the vessel with a point flame near the edge of said window until the photoelectric current reaches a substantially steady value, depositing dielectric material upon said last sodium layer until further increase of photoelectric current ceases, admitting atmospheric air into the vessel, again evacuating the vessel, and again heating the vessel with a point flame near the edge of said window to deposit another layer of sodium upon the last mentioned layer of dielectric material until the photoelectric current reaches substantially a maximum value.
10. A method of making a photoelectric tube comprising an evacuated vessel having an anode and an electrode element comprising photoelectric material, which method comprises increasing the sensitivity of said element by admitting gas containing moisture into said vessel after some of said photoelectric material has been deposited in the form of a layer, re-evacuating said vessel, and again depositing a layer of photoelectric material.
11. A method of making a photoelectric tube comprising an evacuated vessel having an anode and an electrode element made up of intimately

associated layers of photoelectric material and dielectric material, which method comprises increasing the sensitivity of said element by admitting gas containing moisture into said vessel after some of said dielectric material has been deposited upon some of said photoelectric material, re-evacuating said vessel, and forming a thin layer of said photoelectric material on said cathode surface.

12. A method of making a photoelectric cathode which comprises forming a layer of photoelectric material in vacuo, exposing the surface of said layer to a gas which produces thereon a layer of dielectric material, and forming a transparent layer of photoelectric material on said layer of dielectric material.

13. The method of making a photoelectric cathode which comprises forming a layer of sodium material in vacuo, exposing said layer to a gas which produces thereon a layer of dielectric material, and vaporizing some of said material to form an additional cathodic layer.

14. A photoelectric tube including an anode and a light sensitive electrode having a base layer of light sensitive material which is sensitive to visible light, a thin layer of dielectric material thereon, and a thin film of light sensitive material on said dielectric material.

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