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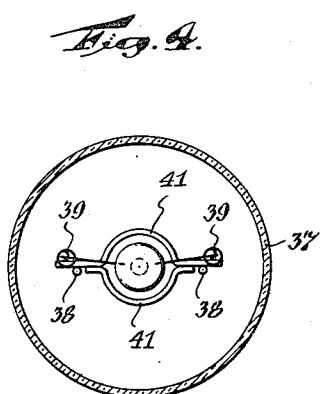
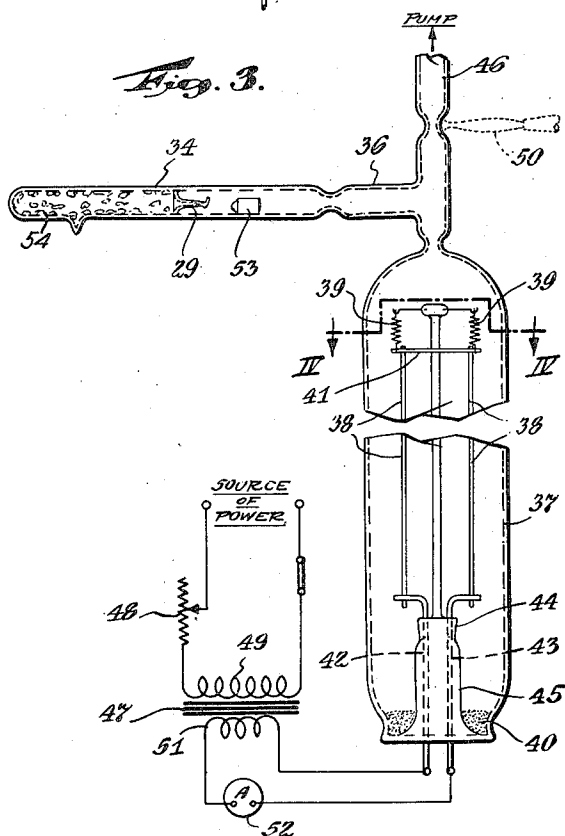
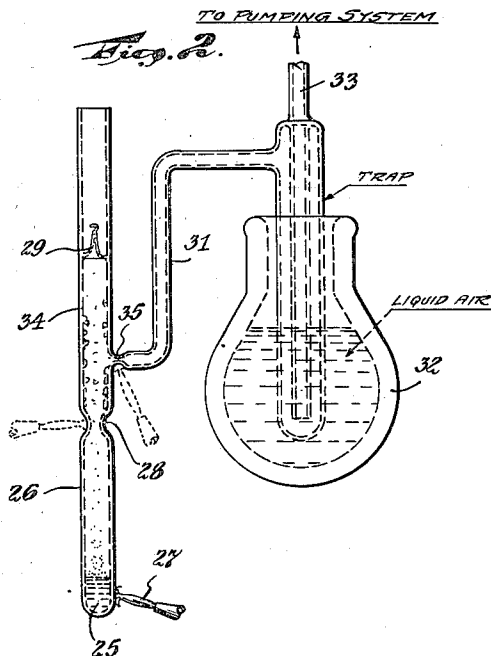
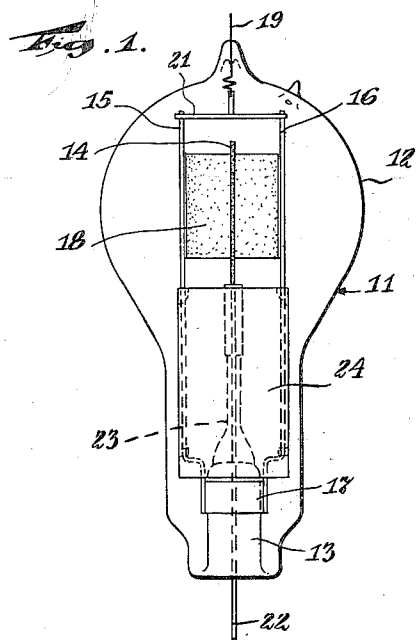
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2,393,264

PHOTOELECTRIC DEVICE AND THE MANUFACTURE THEREOF

Filed Sept. 23, 1942

2 Sheets-Sheet 1



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2 Sheets-Sheet 2

Fig. 5.

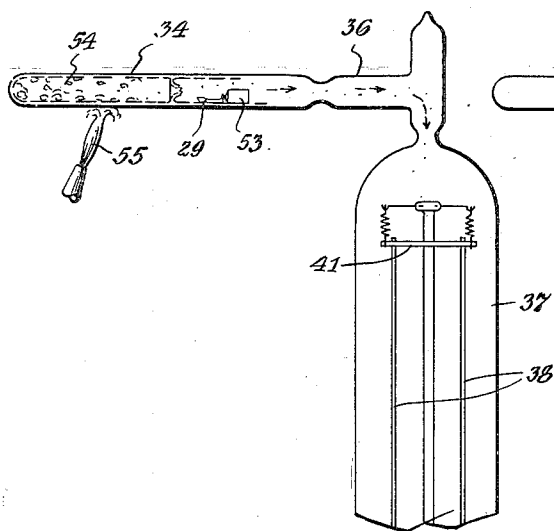


Fig. 6.

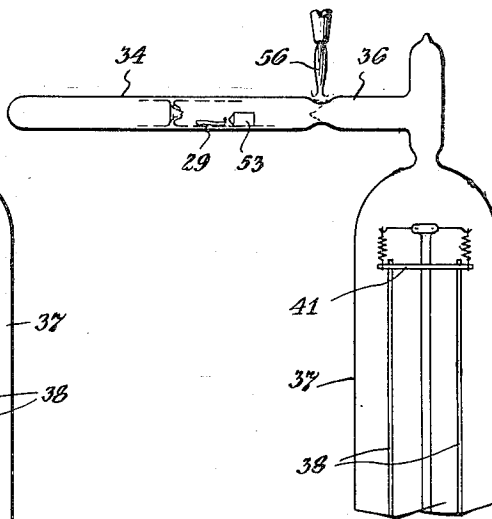
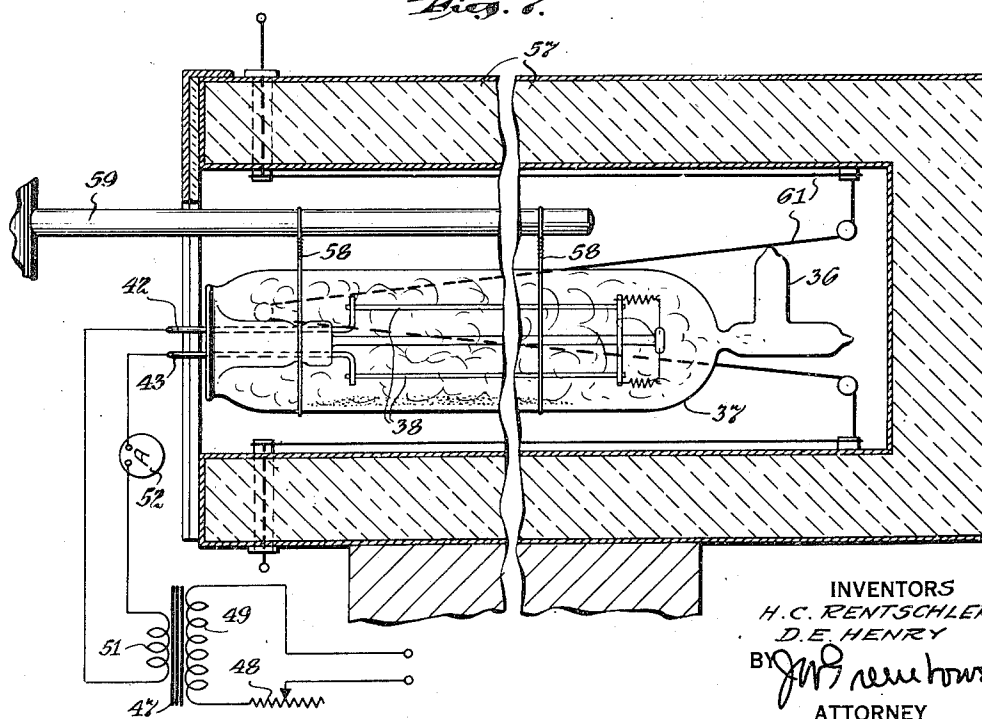


Fig. 7.



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2,393,264

PHOTOELECTRIC DEVICE AND THE
MANUFACTURE THEREOF

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4 Claims. (Cl. 250-165)

This invention relates to photoelectric devices, and, more particularly, to such which are sensitive to radiations in the erythral region of the ultra-violet part of the spectrum.

The principal object of our invention, generally considered, is to provide a photoelectric device for measuring erythral radiation, and in which the photo-sensitive cathode therein consists of zirconium so pure that the results may be reproduced, thereby making the commercial production of uniformly sensitive photoelectric devices practicable.

Another object of our invention is to provide a photoelectric tube which is substantially non-sensitive to the entire visible spectrum but which is particularly adapted for measuring radiation in the erythral range.

A further object of our invention is to produce a photoelectric tube which is sensitive only to ultra-violet light of wavelengths below about 3150 angstrom units.

A still further object of our invention is an improved method of manufacturing a zirconium photoelectric device, including the production of exceedingly pure zirconium for the purpose.

Other objects and advantages of the invention, relating to the particular arrangement and construction of the various parts, will become apparent as the description proceeds.

Referring to the drawings—

Fig. 1 is an elevational view of a photoelectric device embodying our invention.

Fig. 2 is an elevational view of part of apparatus which may be employed in the manufacture of exceedingly pure zirconium for use in connection with the practice of our invention.

Fig. 3 is an elevational view of apparatus in which pure zirconium may be deposited on tungsten wire in practicing the process of our invention.

Fig. 4 is a transverse sectional view on the line IV—IV of Fig. 3, in the direction of the arrows.

Figs. 5 and 6 are fragmentary elevational views corresponding to a portion of Fig. 3, but showing subsequent steps in the practice of our process.

Fig. 7 is a transverse sectional view of an oven in which a portion of the apparatus of Fig. 3 is disposed for effecting the deposition of pure zirconium on heated tungsten wires therein.

In order to measure the effectiveness of ultra-violet radiation in producing erythema, it is desirable that the radiation-sensitive device will not respond to wave-lengths which do not produce erythema. It is further desirable that it responds to different wavelengths to the degree

to which such are effective for the purpose. It is evident from the work of Hausser and Vahle, of Hausser, and of Luckiesh, Holladay and Taylor that the radiation-sensitive device should not respond to wavelengths longer than about 3150 A. U., and that the response should increase rapidly for radiations of shorter wavelengths. A photoelectric tube with a threshold wavelength of approximately 3150 A. U. is, therefore, the ideal radiation-sensitive device provided the response of the tube can be reproduced.

In the Rentschler patent, #1,923,844, dated August 22, 1933, there is disclosed a photoelectric device in which the photosensitive surface is formed of zirconium. This patent was taken out on the zirconium then available. However, further investigation with various metals heretofore obtainable made it apparent that titanium then available came the nearest to fulfilling the desired characteristics for measuring erythral-producing radiations, reference being had to the later Rentschler patent, #1,955,608, dated April 17, 1934, and covering a photoelectric device in which the sensitive surface is formed of titanium.

Considerable difficulty has, however, been experienced in reproducing photoelectric tubes with the same characteristics. This led to the conclusion that the titanium, as commonly produced in the best manner then known, must contain an impurity, either a variable amount of another metal with a longer wavelength threshold, or perhaps a dissolved gas which causes the resultant sputtered film to have a longer wavelength cut-off than that of pure titanium. To further test such a theory, titanium metal prepared in a manner which produced very pure material free from dissolved gas was tried. This metal produced a tube having a threshold wavelength too short to be useful for the measurement of erythral-producing radiations, and further verified the theory as to the presence of an impurity in the titanium previously employed.

We now find that zirconium, prepared by the method to be disclosed, consistently produces tubes having a constant and correct threshold wavelength as required for the measurement of erythral-producing radiation. The zirconium powder, prepared in as pure a state as was heretofore known, is placed in a hard glass or quartz bulb. The bulb has a filament which may be raised to a high temperature by passing electric current therethrough. This bulb is sealed to a high-vacuum pump. To the side of the bulb is sealed a tube containing iodine crystals. The bulb is thoroughly evacuated and baked to as high

a temperature as is safe for the glass while the iodine in the side tube is kept sufficiently cool, as by use of liquid air, to prevent it from volatilizing.

The filament is heated to drive off gases. The bulb is then sealed off from the vacuum pump and the iodine driven from the side tube into the bulb, after which the side tube is sealed off. The bulb is then placed in an oven and heated to between 250 and 350° C., and the iodine combines with the zirconium forming a volatile iodide. The filament is then heated to about 1300° C., and the iodide decomposes, depositing pure zirconium on the tungsten, while the liberated iodine combines with additional zirconium, which in turn deposits. The process is continued to build up a coating of the desired thickness on the filament. Only enough iodine is necessary to combine with a small part of the zirconium powder in the bulb and provide sufficient iodide pressure for good deposition, as the iodine is not used up in the process.

The wire thus built up with a sufficiently thick coating of zirconium can later be used for sputtering the cathode of the photoelectric device with pure metal in order to provide for readily reproducing a cathode sensitive to the desired threshold wavelength.

Referring now to the drawings in detail, the completed photoelectric device is illustrated in Fig. 1 in which the numeral 11 represents a zirconium photoelectric tube as a whole consisting of an envelope 12 of ultra-violet transmitting glass or quartz which is permeable to radiations in the erythral range. Suitable glasses are known to the trade as Corex, Vitaglass and Uviol. However, even glass such as Pyrex may be employed if a thin window is provided for admission of the desired ultra-violet radiation, as described in connection with the Rentschler patents, Nos. 1,923,844 and 1,955,608, previously mentioned.

Inside the envelope 12 is a stem 13 which supports a rod or wire 14, the outer cylindrical surface of which consists of very pure zirconium which may be produced in the manner which will subsequently be described in more detail. The stem 13 has rods 15 and 16 extending from a surrounding collar 17 and holding a substantially semi-cylindrical, preferably nickel, sheet 18 which electrically connects with a lead-in conductor 19 through cross bar 21 between the ends of the rods 15 and 16. The electrode 18 partially surrounds the electrode 14, like the electrode 21 partially surrounds the electrode 2, as shown in Fig. 2 of the Rentschler patent, #1,955,608. Electrode 14 is provided with a lead-in conductor 22 which extends through the press 23 on the stem 13.

A shield 24, like the shield 13 of said Rentschler patent, #1,955,608, is provided and adapted to slide, from the position illustrated in Fig. 1, to enclose the electrodes 14 and 18 during the process of sputtering pure zirconium from the electrode 14 to the electrode 18, to photo-sensitize the latter electrode for measuring erythral radiations. In other words the device 11, illustrated in Fig. 1, may be manufactured like the photoelectric device illustrated in Figs. 1 to 4, inclusive, of the Rentschler patent, #1,955,608, except that the rod 14, from which the photo-sensitive material is sputtered to the plate 18, is formed with a coating of exceedingly pure zirconium free from gases, as in the manner which will now be described. By "exceedingly pure zirconium" we mean such metal containing no material which increases the photoelectric threshold wavelength.

Fig. 2 illustrates apparatus for producing a tube

of pure iodine for use in manufacturing zirconium in accordance with our invention. A quantity of iodine 25 in a tube 26 is distilled by means of fire 27 through a constriction 28 into the upper end portion of a tube 26, which portion is closed by a frangible partition 29, and evacuated through a side tube 31 to a liquid-air trap 32, in order to prevent iodine from reaching the pumping system through exhaust tube 33.

When sufficient iodine has been received in the portion 34 of the tube 26, said tube 26 is tipped off at 28 and the side tube 31 removed therefrom by tipping off at 35. The portion 34 of said tube is then connected to the exhaust tube 36 of the envelope 37, shown in Fig. 3, which contains filaments 38 of tungsten or other refractory metal such as zirconium, tantalum or molybdenum, resiliently mounted, as by springs 39 pulling up on a cross bar or yoke 41 between the upper ends of said filaments, the lower ends of which are connected to lead-in conductors 42 and 43 passing through press 44 of the stem 45 sealed to the lower end of said envelope. The lower portion of the envelope 37 contains a quantity of zirconium powder 46 of commercial purity.

The bulb is then sealed to a vacuum pump through exhaust tube 46, thoroughly evacuated, and baked to as high a temperature as is safe for the glass of the envelope, while the iodine in the outer end of the tube 34 is kept cool to prevent volatilization. During this evacuation the filaments 38 are heated to drive off gases as by means of current from transformer 47 controlled by rheostat 48 in the circuit from source of power through primary winding 49, the secondary winding 51 of which is connected through ammeter 52 to lead-in conductors 42 and 43.

The bulb 37 is then sealed off from the vacuum pump, as by fire 50 illustrated in Fig. 3, and the frangible partition 29 broken, as by means of plunger 53 of iron or other suitable material, and the iodine 54 distilled into the envelope 37 as by means of fire 55, as illustrated in Fig. 5. The tube 34, after removing the iodine, is tipped off from the exhaust tube 36, as by means of fire 56 shown in Fig. 6, and the envelope 37 placed in an oven 57, as shown in Fig. 7, where it may be supported in any desired manner as by means of wires 58 suspended from a rod 59. Said oven may be heated in any desired manner, as by means of a refractory resistance wire 61, in order to raise the temperature of the envelope 37 and its contents to from 250° to 350° C. When so heated the iodine in the envelope combines with the zirconium powder forming zirconium tetraiodide which is volatile.

The filaments 38 in the envelope 37 are then heated to about 1300° C., as by means of the transformer 47 and power source referred to in connection with Fig. 3, whereupon the zirconium tetraiodide vapor surrounding the filaments decomposes, depositing pure zirconium on the tungsten of the filaments, while the liberated iodine combines with more of the zirconium powder to serve as a vehicle for transporting pure zirconium from the powder to build up the thickness of the coating on the filament. Inasmuch as the iodine is released for reuse, after deposition of the combined zirconium on the filament, only enough is necessary to combine with a small part of zirconium powder in the bulb and provide sufficient vapor pressure for good deposition.

When the wire has been built up with a sufficiently thick zirconium coating it is later used as a rod anode 14 in a device such as shown in Fig. 1

for sputtering on a plate cathode 10, or directly on the glass of the envelope, as described in the Rentschler patent, #1,923,844, for producing a cathode of pure metal having a reproducible threshold wavelength.

In view of the foregoing it will be seen that we have disclosed a method of making commercially uniformly sensitive photoelectric tubes for measuring erythema radiations, or those in the ultra-violet region having wavelengths shorter than 3150 A. U. We have also disclosed a method for manufacturing exceedingly pure zirconium, whereby such erythema-measuring photoelectric devices having reproducible characteristics may be manufactured, but we do not wish to be limited to the disclosed method of manufacturing pure zirconium.

Although a preferred embodiment of our invention has been disclosed, it will be understood that modifications may be made within the spirit and scope of the appended claims.

We claim:

1. The method of manufacturing pure zirconium for photoelectric devices comprising placing zirconium powder in an envelope in which is mounted an incandescible tungsten filament, distilling iodine into one end portion of a tube containing a frangible partition intermediate its ends, sealing off said end portion, attaching the other end of said sealed tube to said envelope, evacuating said envelope, sealing off the connection between said envelope and the evacuating means, breaking said partition to provide access between the iodine in said tube and said envelope, distilling iodine from said tube into said envelope, sealing off and removing said tube, heating said envelope to cause the iodine therein to react with the zirconium powder and produce a vapor of zirconium tetraiodide, and heating said tungsten filament to cause deposition of pure zirconium on said filament from said zirconium tetraiodide vapor.

2. The method of manufacturing pure zirconium for photoelectric devices comprising placing zirconium powder in an envelope in which is mounted an incandescible tungsten fila-

ment, distilling iodine into one end portion of a tube containing a frangible partition intermediate its ends, sealing off said end portion, attaching the other end of said sealed tube to said envelope, evacuating said envelope, sealing off the connection between said envelope and the evacuating means, breaking said partition to provide access between the iodine in said tube and said envelope, distilling said iodine from said tube into said envelope, sealing off and removing said tube, heating said envelope to between 250° C. and 350° C. to cause the iodine therein to react with the zirconium powder and produce a vapor of zirconium tetraiodide, and heating said tungsten filament to about 1300° C. to cause deposition of pure zirconium thereon from said vapor.

3. Apparatus for producing pure zirconium for photoelectric devices comprising an envelope containing an incandescible tungsten filament and zirconium powder, a side tube containing iodine in a space separated from that of the envelope by a frangible partition, means for exhausting said envelope while heating the filament, means for breaking said partition and distilling the iodine into said envelope, means for heating said envelope to cause combination between said zirconium and iodine to produce a vapor of zirconium tetraiodide, and means for simultaneously heating the filament to decompose said zirconium iodide with the deposition of pure zirconium thereon.

4. A photoelectric device comprising an envelope transparent to radiations of wave lengths shorter than about 3150 A. U., an anode within said envelope comprising a tungsten core coated with exceedingly pure zirconium deposited within said envelope from the vapor of zirconium tetraiodide, and a photo-sensitive cathode adjacent said anode, said cathode consisting of a nickel plate coated with zirconium sputtered from said anode, whereby photoelectric devices are obtainable, the characteristics of which are reproducible.

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