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PHOTO ELECTRIC TUBE

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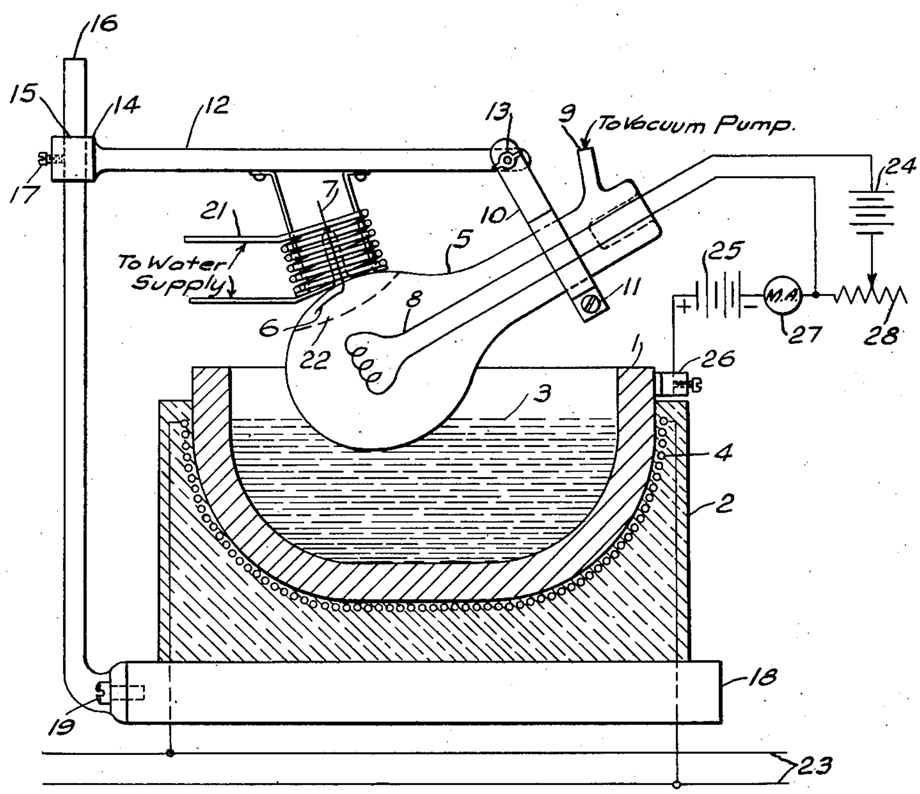

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UNITED STATES PATENT OFFICE

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PHOTO ELECTRIC TUBE

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My invention relates to photo-electric cells, and it has particular relation to methods of supplying such cells with interior coatings of photo-electrically active material.

One object of my invention is to provide a method of applying a coating of a readily oxidizable metal to the interior surface of a container.

Another object of my invention is to provide a method whereby the above described coating may be applied by electrolysis.

Another object of my invention is to provide a method of coating the interior surfaces of containers with a photo-electrically active element.

A still further object of my invention is to provide means for practicing the method referred to above.

It has long been known that, under proper conditions, the alkali metals are extremely sensitive to light, emitting electrons proportionally to the amount of light falling upon them.

The discovery that the hydrides of the alkali metals were still more sensitive to light is generally ascribed to Elster and Geitel, and is fully explained in their article appearing in the Physik. Zeitschrift, Volume XI, 1910. Cells containing potassium hydride as the sensitive element are becoming of increasing importance in a large variety of arts. They are used in alarm systems of various kinds; in telephotography; in systems for the grading of cigars, etc., according to color, and in general wherever it is desired to have some kind of an indication, or record, of varying light conditions.

In so far as I am aware, the majority of the photo-electric cells now on the market are manufactured by a long and tedious process, involving repeated distillation of the potassium in vacuum. The patent to Kunz, 1,381,474, discloses a typical method of manufacture that is quite costly and involves the use of a considerable amount of special apparatus.

According to my invention, the photo-electrically active metal is deposited on the inner wall of the cell by the electrolysis of a salt of the metal, and only exists momentarily as the free element prior to such deposition. In short, I contemplate passing metallic ions directly through the walls of a container, and subsequently causing the metal to be deposited on a desired portion thereof.

For a more complete understanding of my method of forming a photo-electric cell, and of the apparatus used in the practicing of my method, attention is directed to the accompanying drawing, and to the following description.

The single figure of the drawing is a view, partially in elevation, partially in cross-section, and partially diagrammatic, of a preferred form of apparatus used in the practice of my invention.

An iron crucible 1 is supported within a suitable heat-insulating member 2, and contains a mass 3 of molten potassium nitrate, the heat therefor being supplied by a coil 4, or a bunsen burner (not shown). A glass container 5, having an electrode 6, from which a conductor 7 passes to the exterior, a filament 8 and an outlet 9, is held between the jaws of a clamping member 10. The pressure of the clamping member 10 on the glass container 5 is adjusted by the set screw 11. The member 10 is pivotally mounted on a horizontal arm 12, a thumb nut 13 being used to maintain the angular adjustment thereof relative to the horizontal arm.

The horizontal arm 12 is provided at one end with an enlarged portion 14, having an opening 15 therethrough in order to accommodate a vertical rod 16. The portion 14 is slidable on the rod 16, and may be held in adjusted position by a set screw 17. The vertical rod 16 is affixed to a base member 18 by means of a plurality of screws 19, or by other appropriate means. The base member 18 also serves as a support for the heat insulating member 2, and the crucible 1.

A cooling coil 21 is attached to the horizontal arm 12, and is so arranged that it may be positioned in proximity to that portion of the container 5 through which passes the conductor 7.

A coating 22 is shown in the drawing as being deposited on the electrode 6, and on the interior surface of the container 5 adjacent the electrode. The method of obtaining this coating will be fully explained later.

The heating coil 4 is supplied with current from a source 23, while the filament 8 may be supplied with heating current from a battery 24, or a transformer, (not shown) energized from the source 23.

An additional source of potential 25 is included in a circuit between the filament 8 and the iron crucible, contact with the latter being made through a binding-post 26. A milliammeter 27 may be included in the latter circuit, in order that the proper current flow may be maintained, and a rheostat 28 may be used to regulate the filament heating current.

In practicing my invention, the iron crucible is partially filled with anhydrous potassium nitrate, that is caused to fuse together into a molten mass by the application of heat. The mass is preferably maintained at a temperature of approximately 335° C. during the remainder of the process. The glass container is then clamped securely to the support, and the latter is so adjusted that the container is partially submerged in the molten potassium nitrate. The vacuum pump is then started, and the container evacuated to a pressure of 10^{-5} mm. of mercury. As an alternative, the container may be filled with an inert gas, such as argon, at a suitable pressure.

Next, the filament is supplied with heating current at a voltage high enough to cause incandescence, and a relatively high potential is applied between the glowing filament and the iron crucible. As the molten potassium nitrate is ionized, and it is a conductor of electricity, a portion of this potential may be considered as applied across the glass wall of the container, between the potassium nitrate and the filament. To obtain the desired results, the filament is made negative with respect to the molten mass.

Although my invention is not to be restricted to any particular theory of operation it is my opinion that the following action takes place:

Under the influence of the applied potential, potassium ions travel into the interior of the glass wall, and there displace an equivalent number of other potassium ions originally present in the glass. These ions pass to the inner surface of the container, and are immediately neutralized by electrons given off by the incandescent filament, resulting in the momentary presence of metallic potassium. At this inner surface, the temperature is far above the melting point of potassium, 62.5° C. and the potassium is immediately vaporized, to be later deposited on cooler portions of the container. To assure its deposition on the electrode, the latter may be cooled by a coil through which water is caused to circulate, or by equivalent means. In some cases it may not be necessary to employ special cooling means, this of course depending on the size of the container being coated, room temperature, and other variable factors.

The potassium deposits as a dense, coherent mirror, having a high lustre and being quite light-sensitive. If extreme sensitivity is desired, the mirror may be activated by hydrogen, as is familiar to those skilled in the art, after which the tubes may be sealed off in the customary manner.

In the Journal of the Optical Society, July, 1925, R. C. Burt has described a method for introducing sodium into a thermionic tube by means of electrolysis. According to his report, however, he was entirely unsuccessful in passing potassium through the tube walls in the same manner. He attributed this lack of success to the fact that sodium ions are much less mobile than potassium ions, but I have discovered that his negative results and the negative results of other investigators were caused by the differences in the dimensions and the molecular forces of sodium and potassium ions. When a glass containing sodium is used, the potassium replaces the sodium ions, setting up internal strains which tend to shatter the glass.

To successfully pass potassium through the glass wall by electrolysis, I have established the fact that it is essential that the glass be substantially free from sodium.

The glass best suited for the container has been found by experiment to be a variety manufactured by the Corning Glass Company, under the designation G. E. 123 E. This glass contains potassium, less than 1% of lead, and is free from sodium.

Although I have obtained the most consistently reliable results by employing a direct current source for the potential between the filament and the crucible, I have also been able to secure the potassium mirror when alternating potentials are used. When using alternating current, the device itself acts as a rectifier, the path between the filament and the molten potassium nitrate permitting an electron flow only from the filament. Using a current source giving a potential of 110 volts across its terminals, I have been able to pass as high as 200 milliamperes through the glass, but usually a current of 100 milliamperes will be found suitable if over-heating of the glass walls is to be avoided.

My invention, although described herein as specifically adapted to the formation of a mirror of potassium on the inner surface of an exhausted container, is not to be limited to the use of potassium alone, nor is it necessary, in all cases that the container be evacuated. In short, my invention contemplates causing any metal to be driven to the surface of a solid solution thereof, by electrolyzing such solid solution in contact with a bath containing metallic ions, none of which can alter the structural homogeneity of the solid solution when they replace the original metallic ions therein. For example, should it be desirable to obtain a cæsium or rubidium coating on a portion of the interior surface of a glass container, it is preferable that the desired element be the only metal replaced by electrolysis. If other ionizable metals are unavoidably present in the solid solution they should be such that when replaced by ions from the bath no injurious structural alterations are caused.

The principal advantage of my method of making photo-electric cells lies in its relative inexpensiveness. Methods heretofore in use have necessitated the use of elaborate apparatus, and were extremely tedious. It has always been necessary to take extreme precautions to prevent the access of the slightest trace of oxygen to the potassium, compelling a series of re-distillations in vacua. It has also been difficult to satisfactorily govern the amount of potassium used for each individual cell, rendering it practically impossible to produce a plurality of cells having substantially identical characteristics.

By my method, potassium in the metallic state is never exposed to air during the entire operation. Only one vacuum pump is necessary, and the whole series of distillations is done away with. The amount of potassium deposited in each cell may be very accurately determined by the product of the reading of the milliameter in the ionizing circuit and the time during which the container is subjected to the ionizing voltage.

Semi-skilled labor may be employed for every step in the process, with the assurance that the final product will be as good, if not superior to, the product of processes known and pacticed previous to my invention.

Although I have shown and described a specific embodiment of the apparatus to be used in connection with the practice of my invention, other modifications will at once suggest themselves to those skilled in the art. I do not intend, therefore, to be limited except in so far as is necessitated by the prior art, or by the spirit of the following claims.

I claim as my invention:

1. In combination, a container capable of being evacuated and composed of glass containing no sodium, a molten salt of an oxidizable element of the alkali metal group having an atomic weight above 23.05 and means for ionizing said salt and for causing ions to pass through a wall of said container.

2. In combination, a container capable of being evacuated and composed of glass containing no sodium, means for evacuating said container, a molten salt of an oxidizable element of the alkali metal group having an atomic weight over 23.05, means for maintaining the salt in a molten state and means for ionizing said salt and for causing the ions of said element to pass through a wall of the container.

3. A photo-electric cell comprising a glass envelope substantially free from sodium and containing not more than one per cent of lead, potassium ions in a portion of said envelope, metallic potassium on the interior surface of a different portion of said envelope, an electrode within said enevolpe, and inleading wires connected to said metallic potassium and to said electrode.

In testimony whereof, I have hereunto subscribed my name this 11th day of May, 1926.

VLADIMIR K. ZWORYKIN.