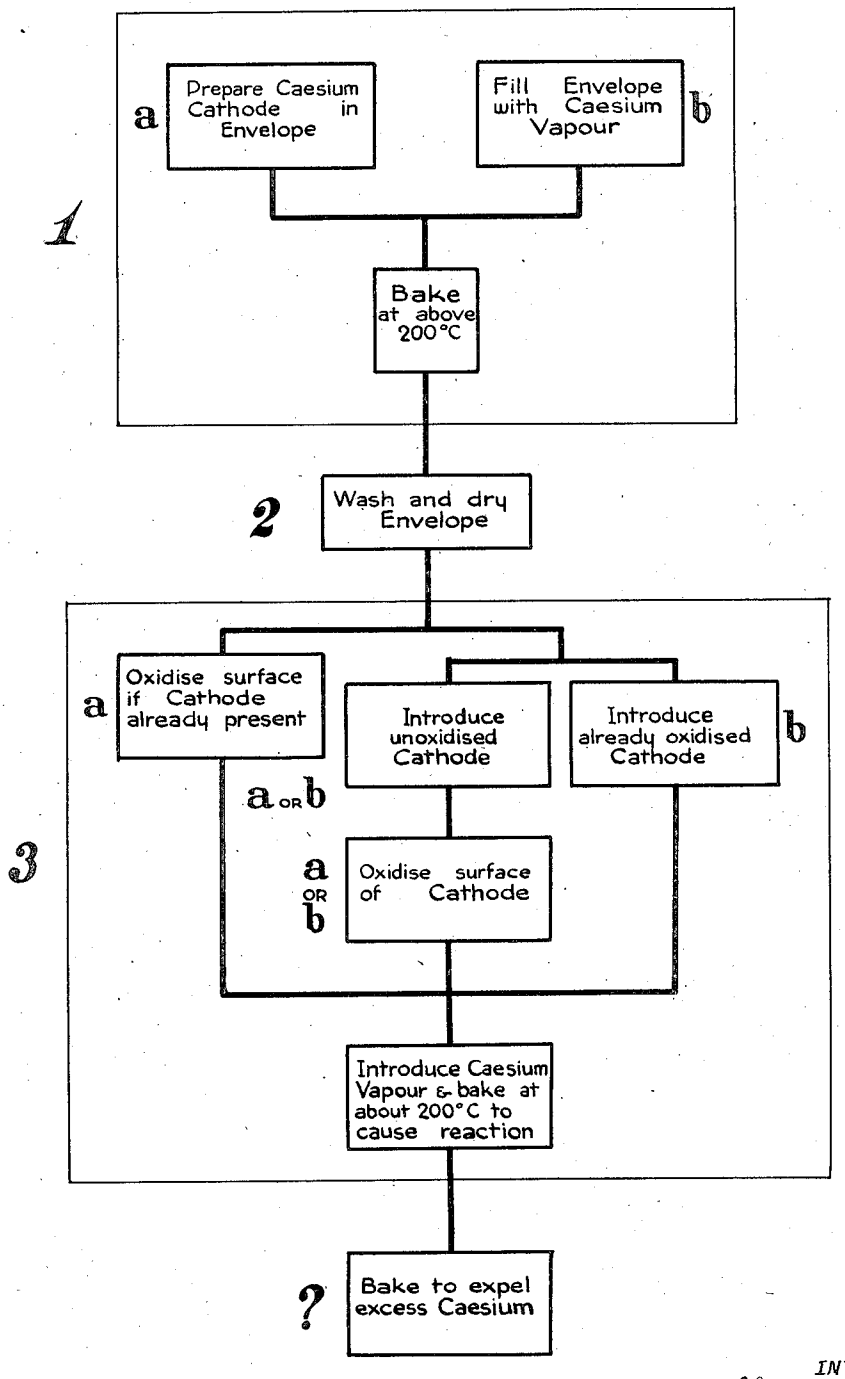
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MANUFACTURE OF PHOTOELECTRIC TUBES

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MANUFACTURE OF PHOTOELECTRIC TUBES

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This invention relates to the manufacture of emission photo-electric tubes having cathodes that are formed by heating, within a vitreous envelope containing caesium vapour, a metal (other than an alkali metal) oxidized at least on its surface. More particularly it refers to the manufacture of what are known commercially as "caesium tubes", having cathodes of which the surface constitution is now often represented by Cs—O—Ag.

The usual method of manufacturing such caesium tubes is to oxidize a silver cathode superficially by a discharge through oxygen, to introduce caesium into the tube, and then to bake the tube to about 200° C., whereby a reaction occurs between the caesium and the oxidized cathode and some or all of the excess caesium is expelled from the tube. It is well known that the emission of cathodes produced by this method is very variable. The object of the invention is to provide a modification of it which yields cathodes whose emission is less variable and is higher on the average than that obtained by the usual methods.

It has been suspected that one cause of the variability of caesium tubes is an attack of the caesium on the glass envelope, whereby substances are liberated which spoil the cathode surface. Hydrogen is likely to be such a substance; for the cathodes are known to be spoilt by minute traces of this gas. If this theory is correct, matters should be improved by attacking the glass with caesium before the manufacture of the tube starts, so that no subsequent attack could occur. But it has not been obvious that there is any stage at which this preliminary attack can be conducted. If caesium is introduced when the tube is already pumped and before oxidation of the silver, it alloys with the silver and prevents satisfactory oxidation afterwards. If the treatment is effected before the tube is finally pumped, it would not be expected to survive exposure to the air.

I have discovered a process for improving the emission of tubes which, if it is to be explained at all on the foregoing theory, shows that this last expectation is false. The invention, consisting of a process, is independent of any explanation of the effect of the process; and it is possible that the ideas which led to its development are wrong. Nevertheless they are useful in relating the invention to the prior art.

According to the invention the manufacture of emission photo-electric tubes comprises the following steps in the order indicated, namely (1) exposing the interior surface of a vitreous envelope to attack by a caesium containing substance, (2) washing the interior of the said envelope with a liquid adapted to remove caesium compounds soluble in water, but not adapted to remove compounds soluble only in hydrofluoric acid, and then drying the said interior, (3) forming within the said envelope a photo-electric cathode by heating within the said envelope, when containing caesium vapour, a metal (other than an alkali metal) oxidized at least on its surface.

The accompanying drawing shows the relation between the steps according to the invention. The outer rectangles numbered **1**, **2**, **3** represent the aforesaid three steps. The inner rectangles within outer rectangles **1** and **3** represent various alternative methods of carrying out these steps, which will be explained further presently. If alternative "*a*" is adopted in **1**, an alternative "*a*" must be adopted in **3**; if alternative "*b*" is adopted in **1**, an alternative "*b*" must be adopted in **3**. The lowest rectangle, marked "?", represents a step that is usually part of the normal manufacture of these photo-electric tubes; but it is not absolutely essential, and, at any rate, forms no part of the invention.

In one method of manufacture according to the invention a tube is prepared by the usual method hereinbefore described and sealed off from the pump. It is then baked for several minutes at a temperature considerably exceeding 200° C. If the envelope is of borosilicate glass, 400° C. is an appropriate temperature. The tube is then opened and washed out with water; if the silver is a layer in the walls, it is dissolved off with nitric acid. If the temperature and time of the baking have been sufficient, the walls will be found to be attacked; they will be imperfectly smooth and a layer of silver deposited on them chemically will no longer be perfectly bright. The baking must always be sufficient to produce this attack; but so long as it is produced, the exact temperature and time of attack are not very important.

The tube is now re-made in the same way as before. The emission of such tubes remade after being baked is more uniform and higher on the average than tubes made for the first time. It may sometimes be desirable to bake the tube again and make a third time; it is seldom necessary to repeat the process oftener. This is the alternative "*a*" represented in the diagram.

According to the tentative explanation that has been offered, the envelope has been attacked

during the bake by caesium or caesium compounds within the tube, so that a layer has been formed which prevents further attack. The protective layer survives washing with water or nitric acid. It is destroyed, however, by washing with hydrofluoric acid; for tubes re-made after such washing seem no different from new tubes.

In the foregoing method, one part of the final cathode, namely the silver that is afterwards oxidized, is introduced into the tube before the attack on the envelope.

In an alternative, and usually preferable method, the attack on the envelope is caused to take place before the introduction of any part of the cathode. In this case metallic caesium is preferably used as the attacking agent. Thus the envelope containing the anode, but not the other electrode, may be evacuated and sealed off with a little caesium inside. It is then baked, so that the caesium attacks the glass. The attack does not now affect materially the polish of the glass; but if it proceeds far enough, the glass will be coloured. The attack is preferably stopped just before visible colouration appears. But the desired effect is sometimes obtained when the effects of the attack are apparent only to microscopic or delicate colorimetric examination. If the glass is soda-lime, baking at 400° C. for 50 minutes is sufficient; if the glass is borosilicate a higher temperature or a longer time must be used, for example 2 hours at 400° C. The envelope is then opened and washed with water. A silver electrode, which is to carry the cathode, is now introduced, either by silvering the wall or by introducing a silver plate supported out of contact with the walls. It is oxidized and heated in the caesium vapour in the usual manner, to form the cathode. It is possible, however, when a silver plate is to form the cathode, to oxidize the plate outside the envelope, introduce it into the envelope and then heat in caesium vapour. These are the two alternatives "b" represented in the drawing.

I have tried to improve caesium tubes by substituting an alkali other than caesium, e. g. rubidium, for caesium during the step that is characteristic of the invention. But no success has been attained. I have also tried to improve tubes in which caesium is replaced by another metal in the cathode, e. g. rubidium or potassium tubes, by a preliminary attack on the glass. But they also have led to no definite result, perhaps because such tubes are less liable to the variability which it is the object of the invention to cure.

I claim:—

1. In the manufacture of photo-electric tubes having a vitreous envelope, the process which includes introducing caesium into the envelope and sealing off the tube, then heating the tube to vaporize the caesium and effect a modification of the inner wall of the envelope by the action of caesium vapors thereon, opening the tube and washing out the envelope with an aqueous solution which will not affect the modified inner wall thereof, drying the interior and then completing manufacture of the tube.

2. In the manufacture of photo-electric tubes having a vitreous envelope, the process which includes introducing caesium into the envelope and sealing off the tube, then baking the tube to vaporize the caesium and cause its vapors to attack the inner wall of the envelope so as to modify the same, opening the tube and washing out the envelope with a suitable solvent for caesium and its compounds which will not affect the modified inner wall of the envelope, drying the interior thereof and thereafter completing the tube and sensitizing the cathode element with caesium.

3. In the manufacture of photo-electric tubes having a vitreous envelope, the process which comprises introducing caesium into the envelope, sealing off the tube and baking it to cause caesium vapors to effect a modification of the inner wall of the envelope, opening the tube and washing out the interior with a suitable solvent for caesium and its compounds which will not affect the modified inner wall of the envelope, drying the interior, then introducing an oxidized metal cathode element and again introducing caesium, and baking the tube to complete the formation of the cathode.

4. In the manufacture of photo-electric tubes having a sealed vitreous envelope containing caesium in vaporizable form, the process which includes baking the tube at a temperature considerably in excess of 200° C. to vaporize the caesium and cause its vapors to attack and effect a modification of the inner wall of the envelope, opening the tube and washing out the envelope with an aqueous solution which will not affect the modified inner wall thereof, then drying the interior and thereafter completing the manufacture of the tube in the usual way.

5. In the manufacture of photo-electric tubes having a sealed vitreous envelope containing a cathode element formed with a caesium sensitized surface, the process which comprises baking the tube for a predetermined time at a temperature in excess of 200° C. to vaporize the caesium and cause its vapors to effect a modification of the inner wall of the envelope, then opening the tube and washing out the interior of the envelope with a solvent for caesium and its compounds which will not affect the modified inner wall of the envelope, drying the interior thereof and thereafter remaking the tube in the usual way.

6. In the manufacture of photo-electric tubes, having a vitreous envelope, the process which comprises introducing vaporizable caesium material into the envelope, sealing off the tube and baking it for a predetermined time at a temperature in excess of 200° C., to vaporize the caesium and cause its vapors to effect a modification of the inner wall of the envelope, opening the tube and washing out the interior with a suitable solvent for caesium and its compounds which will not affect the modified inner wall of the envelope, drying the interior, then introducing an oxidized silver element for forming the cathode and introducing caesium, then heating the oxidized silver element at a temperature of approximately 200° C. for completing and sensitizing the cathode.

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