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HIGHLY EMISSIVE CATHODE

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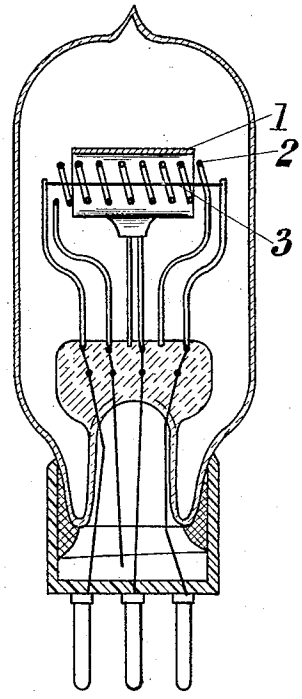

Fig. 1.

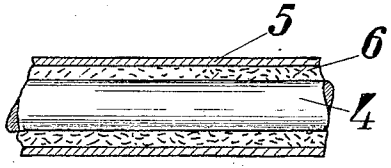

Fig. 2.

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UNITED STATES PATENT OFFICE

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HIGHLY EMISSIVE CATHODE

Application filed June 22, 1931, Serial No. 545,998, and in Germany June 25, 1930.

The invention relates to a highly emissive cathode and a method of producing the same, more particularly according to the metal vapour process. In cathodes which are produced according to this method, for example by the fine application of barium vapour to a cathode composed of another material, the extremely high emission of the applied barium is based on the co-operation of a number of factors, which in themselves have not as yet been fully accounted for, but in which a temporary oxidation of the barium appears to have considerable bearing. The conditions are possibly such that electrolytical or similar conversions occur between metallic barium and barium oxide in the known valves with barium emission, and that the electronic emission takes place upon a reaction of this kind, for example upon the oxidation of the barium or the reduction of the barium oxide. It has also been shown that heretofore certain substances have always been present permitting of the oxidation of the barium. It was shown, for example, that tungsten filaments, which contain certain oxides, are quite particularly adapted to serve as body materials for highly emissive barium cathodes.

The invention relates to another method of activating the barium emission which has proved to be of advantage, and which, according to the tests hitherto carried out, would appear to be superior in many respects to the formation by oxidation.

It is unnecessary for the barium to be oxidized. In addition to barium oxide other barium compounds have proved to be at least equivalent in an electrical respect, while these barium compounds of other kind disclose advantages both as regards the method as well as certain conditions of emission.

According to the invention, compounds of that kind are employed on the cathode which do not contain the metal in combination with oxygen alone (or, which in a certain respect is equivalent thereto, in combination solely with a hydroxyl group). Barium sulphide BaS or barium cyanide ($Ba(CN)_2$) are examples of those compounds which result in the necessary mutual decompositions with the barium. The electrical conductivity, which more particularly in the case of barium sulphide is greater than that with barium oxide, is apparently the reason for more favourable emissive conditions.

The invention will therefore be described in the following with the assistance of a few examples based on the use of barium sulphide on the cathode. The most simple embodiment of a method of production of cathodes of this description would consist in applying barium sulphide to the cathode in direct fashion, and thereupon atomizing barium on to the cathode in any suitable manner known per se. In place of the direct employment of barium sulphide it may be desirable to introduce sulphur vapour in minute amount, either prior to or immediately after the atomization of the barium, in order to thus obtain the formation of sulphide.

According, however, to the additional subject matter of the invention, the sulphide is produced on the cathode itself. In this manner gas-technical, vacuum-technical and other difficulties in manufacture are avoided.

It is known in itself that barium sulphide, BaS, is obtained by the reduction of barium sulphate, $BaSO_4$. If now barium sulphate is applied to the filament, and on the other hand, in the manner known per se and customary in respect of the metal vapour process, barium is so atomized within the valve that the same is deposited preferably on the filament, this barium itself will act as reducing agent in face of the barium sulphate, possibly according to the following formula, which is at least correct in the final result:

$$BaSO_4 + 4Ba = BaS + 4BaO.$$

The invention is not limited to the use of barium alone. Similar substances may also

be employed as emissive metals for performing the metal vapour process and as cations for the sulphate. Thus, for example, potassium sulphate is more suitable than barium sulphate for application to the cathode, particularly if the same is employed in the form of potassium bisulphate, $KHSO_4$, which possesses a considerably lower melting point than neutral potassium sulphate.

Good results are accordingly obtained with a cathode produced in the following manner:

A tungsten filament was in the first place conducted through molten potassium bisulphate produced at 270–300°, so that the same was coated therewith on the surface. After setting the filament in the system and fitting the system in the valve, the hydrogen was removed from the sulphate, for example during the pumping operation, by heating the filament, so that as a whole merely normal sulphate apparently remained on the filament surface. Barium was thereupon atomized on to the cathode, a barium oxide and aluminium mixture being applied laterally of the cathode and heated to the extent of aluminothermal reaction. The barium deposited on the cathode will undoubtedly have reduced the potassium sulphate. Presumably there is formed in this connection an equilibrium of potassium sulphide K_2S, barium sulphide BaS, barium oxide BaO and potassium oxide K_2O, in the presence of a considerable excess of metallic barium.

The smallness of the amounts decomposed upon these reactions, and in part only requiring to be present in layers of atomary thickness, did not permit of investigations as to whether all of these assumed components of the reaction actually occurred. It is in any case quite certain that cathodes produced according to the method described disclose an admirable barium emission, without in this connection there being necessary as a particular step in the method the oxidation particularly made use of in the usual process.

A further embodiment of the process according to the invention may consist in sulphurating the applied barium by the introduction of small quantities of sulphuretted hydrogen. In this case there is formed barium sulphide, while upon the degasifying process not only the excessive sulphuretted hydrogen but also the gases, such as hydrogen, formed upon the reaction may be pumped away. The method is performed in the most suitable manner by at first atomizing a small quantity of barium on to the cathode, then introducing a small quantity of sulphuretted hydrogen, for example from a sulphuretted hydrogen container, which by means of a three-way tap is connected in a manner permitting the same to be readily shut off with the pumping socket of the discharge vessel. After the introduction of the sulphuretted hydrogen and the subsequent removal of the excess by pumping, the valve is preferably first sealed and then barium again evaporated, viz., at this stage the essential part of the barium.

Those electrodes which are not desired to perform emission, i. e., in normal three-electrode valves all electrodes with the exception of the cathode, are in this case preferably produced from a metal of that kind which is not, or only to the least possible extent, attacked by the sulphuretted hydrogen.

Admirably adapted for this purpose is molybdenum, which in itself is already employed as a material for the grids, but which in the present case, according to the additional subject matter of the application, also enters with advantage into consideration as regards a material for the anode. Tungsten may also be employed for electrodes of this kind, whether the same is pure or in the form of an addition or accompanied by additions, which should not be attacked in carrying out the process according to the invention.

An additional embodiment of the invention consists in introducing sulphur dioxide SO_2 into the valve. This possesses in comparison with sulphuretted hydrogen the advantage of not being so very highly reactive. The same does not attack the metals in the valve with the same readiness. It is possible, for example, without difficulty, to employ nickel electrodes, and more particularly nickel anodes, in those valves into which sulphur dioxide is temporarily introduced in performance of the process according to the invention. The sulphur dioxide is mutually decomposed with barium oxide in such fashion that equilibrium exists between these two substances on the one hand and barium sulphate and barium sulphide on the other hand. In turn the barium sulphate, in the manner set forth at the commencement, results by reason of reduction by metallic barium in barium sulphide and new barium oxide. Small amounts of barium oxide, which initially are always present if due only to inexactitudes or leakages of the apparatus, are accordingly sufficient to create fresh quantities of barium oxide which, for the additional course of the process, are essential for maintaining the formation of barium sulphide (in addition to barium oxide) from barium and sulphur dioxide.

Altogether, there accordingly results from the two reactions, viz.,

$$(1)\quad 4SO_2+4BaO=BaS+3BaSO_4$$

and

$$(2)\quad BaSO_4+4Ba=BaS+4BaO$$

a mutual decomposition according to the total equation

$$(3)\quad 3Ba+SO_2=BaS+2BaO$$

In this manner there accordingly results

a cathode which, in addition to barium sulphide, also contains barium oxide. It would seem, however, that the barium sulphide, due to its greater conductivity, also in this case plays a predominating part in the electronic emission. The invention has been described substantially with the assistance of a few examples of the metal vapour process, which refer to the use of barium cathodes, because among the metal vapour cathodes these are the most important. The invention, however, is not restricted thereto, and may, with correspondingly adapted possibilities of reaction, which in part are somewhat different in the case of the other materials, be applied to cathodes making use of other light metals, more particularly cathodes composed of calcium or strontium.

The invention has also been more particularly described with the use of bivalent sulphur as electron transmitter. To this the invention is also in no way confined.

The invention is illustrated by the accompanying drawing in which Figure 1 shows an electron discharge device containing a plate 1, a grid 2 and a cathode 3. A longitudinal section through this cathode 3 is shown on a larger scale in Figure 2. The cathode consists of the cathode body 4 i. e. a wire of tungsten or like metals and the actual emissive layer 5 for instance of barium. Between the wire 4 and the layer 5 an intermediate layer is provided consisting each according to the selection of the starting material of barium sulphides, barium oxides, etc.

I claim:

1. A method for manufacturing highly emissive cathodes which consists in coating the surface of the cathode body with a compound of sulphur with a highly emissive metal and that thereon a highly emissive substance is deposited in form of metal vapour.

2. A method for manufacturing highly emissive cathodes which consists in coating the cathode body with a compound of sulphur with a highly emissive metal adapted to produce by reactions sulphides of said highly emissive metal and that thereon a highly emissive substance is deposited in form of metal vapour.

3. A method for manufacturing highly emissive cathodes which consists in coating the cathode body with a compound of sulphur with earth-alkali metals adapted to produce by reactions sulphides of said earth-alkali metals and that thereon a highly emissive substance is deposited in form of metal vapour.

4. A method for manufacturing highly emissive cathodes which consists in coating the cathode body with a sulphate of earth-alkali metals and that thereon a highly emissive substance is deposited in form of metal vapour.

5. A method for manufacturing highly emissive cathodes which consists in coating the cathode body with a barium sulphate and that thereon a highly emissive substance is deposited in form of metal vapour.

6. A method for manufacturing highly emissive cathodes which consists in coating the cathode body with a barium sulphate and that thereon barium is deposited in form of vapour.

In testimony whereof I have affixed my signature.

OTTO EMERSLEBEN.