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ACTIVATING MATERIAL FOR ELECTRODES IN  
ELECTRIC DISCHARGE DEVICES  
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Fig. 1

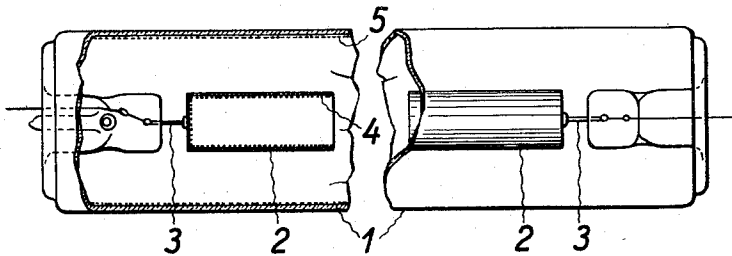


Fig. 2

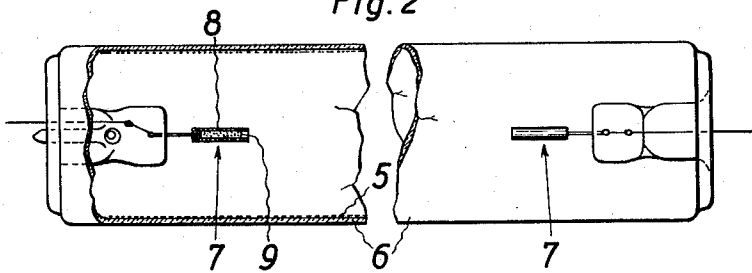
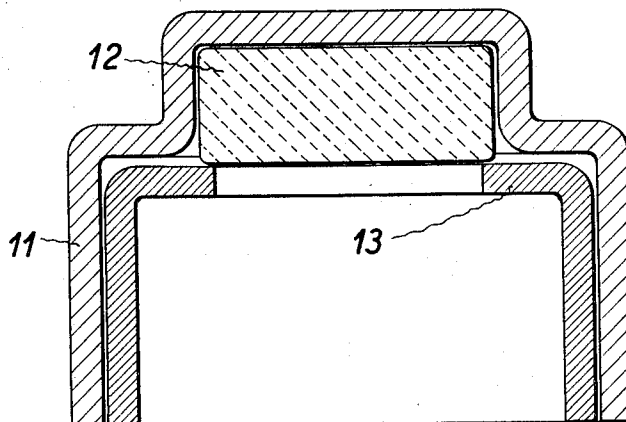


Fig. 3



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## ACTIVATING MATERIAL FOR ELECTRODES IN ELECTRIC DISCHARGE DEVICES

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5 Claims. (Cl. 252—521)

The present invention relates to an activating material for electrodes in electric discharge devices being filled with gases, vapours or gas-vapour-mixtures, especially in low pressure fluorescent tubes or -lamps in which the cathode fall of the electrodes shall be reduced as much as possible without impairing the quality of the lamp by a gas development of the electrodes, by spotting and darkening the luminescent coating.

Heretofore used, well-known activating materials, such as barium- or strontium-oxides, applied to the electrodes by suspending or similar methods, have caused already a good emission of electrons and consequently a reduction of the cathode fall, but often they have had the disadvantage of easy sputtering and undesired spotting of the tube wall and blackening the luminescent coating which has been the case especially in so-called cold cathodes, for instance of iron-sheet metal cylinders. The oxides of the activating metals as barium oxide and strontium oxide are produced by thermic treatment from other compounds of the alkaline earths, for instance from carbonates or from the super oxides after their introduction into the discharge devices. Using cold cathodes the thermic treatment of the carbonates takes place by increased discharge currents on the electrodes, e.g. on the iron cylinders. The required glow temperature of more than 1000° C. cannot be reached in consequence of the easy vaporizability and danger of sputtering so that, therefore, often a complete decomposition of the carbonates and an insufficient activation result. Carbonates being incompletely decomposed may cause during the burning hours of a lamp the already mentioned gas development of the electrodes, spotting and darkening of the luminescent coating, e.g. because mercury compounds are formed.

Accordingly, an object of this invention is that activating materials and methods of their manufacture have been discovered which do not have the above described disadvantages, but have a durable partly reduced conductive form in the air and a good ability to adhere. The activating material according to this invention consists completely or partly in a partly reduced chemical compound of an oxide of an alkaline earth metal with an oxide of rare earths, especially Ce, or of Sn or Ti respectively or of a mixture of the oxides of the said elements. The activating material contains preferably barium-cerate, BaCeO<sub>3</sub>, which particularly has a perovskite structure. The activating material is suitably produced as a semi-conductor by thermic reducing treatment, preferably in hydrogen outside the discharge device. Reduced BaCeO<sub>3</sub> has a durable, partly reduced conductive form in the air, similar to titanates crystallizing in perovskite lattice too. For example activated BaO is not stable in the air because it is able to react with oxygen or carbonic acid respectively or with water vapour, whereas for instance activated BaCeO<sub>3</sub> does not change its stability in the air at normal temperatures. According to this invention the activated state may be impressed to the material by reducing firing from the

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first. By that means the firing times are shortened at the manufacture of the tubes. For the purpose of accelerating the activating process according to further ideas of this invention preferably suitable reducing metal powders in small quantities are admixed to the activating material, preferably an air stable alloy of 50% Al and 50% Ba in quantities of 1 to 10%, preferably of 3%. At a too great surplus there is the risk of vaporizing metallic Ba which will cause spotting. The forming of the electrodes will be very much facilitated because these additions of getter metals are gettering away any oxygen adhering to the material. Preferably the method of manufacture of the activating material according to this invention will be in such manner that the oxide of an alkaline earth metal is mixed well together with an oxide of rare earths, especially Ce, or of Sn or Ti respectively, or with a compound of the oxides of said elements or with an alkaline earth compound which delivers, when being heated, a corresponding oxide in the same mol ratio, e.g. 1 mol CeO<sub>2</sub> with 1 mol BaCO<sub>3</sub> ground and fired at 1200 to 1400° C. in air for about 2 to 3 hours. At the manufacture of barium cerate the nearly white cerate only a little coloured is produced according to the equation  $\text{BaCO}_3 + \text{CeO}_2 \rightarrow \text{BaCeO}_3 + \text{CO}_2$ . Then the material will be once more ground in dry state and thereupon shortly, say for ½ hour, fired at about 1400° C. The stable compound received by such manner will be transformed suitably to the activated semi-conducting state by further firing at about 1000° C. in a hydrogen stream. According to the time of reduction there are to be obtained compounds with less or more semi-conductive qualities; especially the absolute value of the conductivity as well as the dependency upon temperature and consequently the activating state of the cerate may be regulated as desired.

Preferably an activating material will be used which consists only of the partly reduced Ba-cerate according to this invention. The idea of this invention is also used when employing any activating material according to this invention containing also other activating substances already known though the above mentioned bad influences are present partly.

The electric conductive state of the BaCeO<sub>3</sub> which is necessary for a good thermic emission being produced when firing in H<sub>2</sub> is stable at normal temperatures; but this state will be more or less annulled by reoxidation if the partly reduced BaCeO<sub>3</sub> material will be exposed to higher temperatures (>200°) in air which is the case for instance at sealing-in the stems into the discharge tube which are bearing the electrodes if there are taken no special precautions, as perhaps nitrogen washing. But the consequence of such a reoxidation of the partly reduced BaCeO<sub>3</sub> is such that the electrodes must be heated more or less by discharge current in the discharge tube subsequently for the purpose of forming.

Now it has been discovered that this reoxidation of the partly reduced BaCeO<sub>3</sub> will be prevented if this compound is a so-called controlled valency semi-conductor.

A good semi-conductivity and thermic emission will be reached according to this invention with regard to the barium cerate by replacing a part of the O<sup>2-</sup> -ions by F<sup>-</sup> -ions (a part of the double negative loaded oxygenions by single negative loaded fluorine ions) without changing hereby the compound in its crystal lattice structure. By this manner a compound will be reached of the kind BaCe (O<sub>3-δ</sub>, F<sub>δ</sub>) with δ ≤ 1. It is the advantage of such a fluorine containing cerate that also at stronger heating in air (about 400° C.) a reoxidation and consequently a destruction of the conductivity will not arise. By this manner it will be reached to facilitate very much the exhausting of discharge tubes with fluorine-containing cerates as cathode material because no foreign

gases in a disturbing quantity are developed and because a stronger heating of the electrodes is not necessary.

The fluorine-containing Ba-cerates will be produced most suitably by firing a compound of 1 mol  $\text{BaCeO}_3$ , produced according to the above mentioned method, with  $x$  mol  $\text{CeO}_2$  and  $x$  mol  $\text{BaF}_2$  whereby  $x$  may be 0.01 to 1, preferably 0.1 to 0.3, for 2 to 3 hours in  $\text{H}_2$  at 1350 to 1400° C. A good mixing of the materials is necessary which will be reached in the best way by grinding in the ball mill. A further method of manufacture is to fire 2 mol  $\text{BaCeO}_3$  with  $x$  mol  $\text{BaCO}_3$  and  $x$  mol  $\text{CeF}_3$  under the same conditions whereby  $x$  may again vary within the above mentioned limits. According to both the methods a dark coloured crystalline material with perovskite lattice structure will be obtained.

An activating material is suitably used in the form of an emulsion of the finest ground activating powder in alcohol, acetone, butylacetate or other suitable organic liquids without or with organic binders as coating paste for cold cathodes or hot cathodes in low pressure discharge lamps. As it is already to be seen from the above description, it has proved good to use barium cerate especially for cold cathodes because the firing process by means of discharge current heating is omitted which only is to be regulated with difficulties. The reduction of the cathode drop to be obtained is as great with the  $\text{BaCeO}_3$  and with the  $\text{BaCe}(\text{O}_{3-x}\text{F}_x)$  as with the best oxide pastes. The cathode drop amounts in both cases to about 85 to 95 volts. But also when using hot cathodes the  $\text{BaCeO}_3$  has real advantages. For instance the ability of the cerate to adhere on the metallic bases, e.g. tungsten coils, is greater than that of the  $\text{BaO}$  which is very much loosened in consequence of the gas development during the thermic decomposition of the carbonates. The cathode drop of the cerate in the hot cathode is also of the same size as that in the best oxide hot cathodes. It lies between 10 and 15 volts.

The barium cerate may be used also in the form of sintered compact pieces (rods) with or without metallic enclosure as hot cathode (supply cathode) in discharge devices. This form proved very suitable for cold starting slimline lamps because the material hardly sputters and as shown by tests can endure more than 400,000 cold startings. Besides, it is an advantage that no binders, e.g. nitrocellulose etc., are to be employed which always would involve impurities by coal residues or carbon compounds at decomposition.

Further advantages of the activating material according to this invention follow from the method of manufacture. A thermic decomposition is not necessary so that a generation of gas will be avoided in the discharge device. Therefore, no loosening of the layers arises caused by the generation of gas, as in the case of  $\text{BaO}$ . The life of the cerate cathode is very good because the stability of the  $\text{BaCeO}_3$  and especially that of the  $\text{BaCe}(\text{O}_{3-x}\text{F}_x)$  is great and because the speed of evaporation is reduced in consequence of forming compounds. Owing to the fact that no decomposing gases are generated when using Ba-cerate the spotting, caused often by uncomplete decomposition when using  $\text{BaCO}_3$  or  $\text{BaO}_2$ , and the darkening of the luminescent layer, because a mercury compound is formed, are prevented. The decrease in the brightness during life, especially in luminescent tubes, is much lower than in tubes having otherwise activated electrodes.

Referring to the drawing:

Figure 1 is an elevational view, with parts in axial section, of a discharge device embodying my invention.

Figure 2 is a view similar to Figure 1, but showing a modification.

Figure 3 is a much enlarged axial sectional view of a modified form of electrode, which may be used in a discharge device such as shown in Figure 1 or Figure 2.

Some kinds of cathodes in discharge tubes with the activating material according to the invention are shown

in the drawing as examples. Fig. 1 shows a discharge tube 1 of glass on each end of which an electrode 2 is provided consisting of an iron sheet metal cylinder closed as usual on the one side. The leading-in wires 3 of the electrode cylinders 2, serving likewise as supports for them, are also sealed-in in the stems of the discharge tube in a well-known manner. The inner wall of the electrode cylinder is coated with an activating material 4 according to this invention, e.g. barium-cerate ( $\text{BaCeO}_3$ ), which is applied to the wall of the electrode in the form of an emulsion in alcohol. The discharge tube 1 is filled with rare gas, e.g. argon, and may contain a bit of mercury. In our example the inner wall of the discharge tube is still provided with a luminescent layer 5, e.g. of Mg-wolframite, Zn-Be-silicate or of any mixture of luminescent materials, to obtain the color radiation desired. The gas pressure may be about 4 to 3 millimeters and the current intensity of the surface of the electrodes about 20 ma./cm.<sup>2</sup> and more. A hollow cylinder electrode may be loaded with about 200 ma. and more if it is closed at the one end and having a diameter of 10 mm. at a length of 30 mm. and an activating material according to this invention, e.g.  $\text{BaCeO}_3$ , on the inner wall.

Fig. 2 shows a discharge tube 6 with hot cathodes 7 (one of them in sectional view) consisting of little hollow metal cylinders 8, e.g. of molybdenum or nickel, in the inner space of which is to be found the activating material 9 according to this invention, e.g., barium-cerate, in the form of strong compressed powder or in the form of a suitable sintered cerate pill. The metallic cylinders 8 may have for instance a length of 10 mm., an inner diameter of 1 mm. and a wall thickness of 0.1 mm. The current loading power of these electrodes operating already at small surges (of about 100 ma.) as hot cathodes may vary within the limits of about 150 to 500 ma. The discharge moves completely into the inner space of the electrodes. The metallic cylinder itself does not glow or only a little during operation.

The current loading power of the electrode towards smaller or greater currents over the above mentioned current loading may be still increased by changing the diameter and the wall thickness of the metallic cylinder towards smaller or greater values than stated. The cathode drop lies at 16 volts at currents of 150 ma., at about 12 volts at currents of 500 ma. The gas filling of the discharge tube may here also amount to about 4 to 8 millimeters and the inner wall may be provided with a luminescent coating 5 according to the example given in Fig. 1.

Fig. 3 shows a further modified form of a cathode with the activating material according to this invention in a very much enlarged scale of 20:1. The fluorine-containing barium-cerate body 12 according to this invention is provided in a metallic electrode cap 11. In our example the barium-cerate body 12 fits into a groove of the electrode cap 11 and is held by a metallic holding body 13. The electrode cap 11 suitably fits with the opening towards the stem of the lamp which is not shown in the drawing. The dimensions and accommodations of the activating material of the form of the electrodes etc. may be similar to those as shown in the examples of the Figs. 1 and 2. The electrode cap 11 may have for instance a diameter of 5 mm., a length of 4 mm., and a height of 1 mm. at the groove. The loading power of these electrodes, operating also as hot cathodes already at small currents (of about 150 ma.), may vary within the limits of about 150 to 500 ma. The discharge moves completely into the inner space of the electrodes. The metallic cylinder itself will not glow or only a little during operation. The metallic holding body 13 may favourably consist of thin molybdenum sheet because it rises to higher temperatures.

The inner wall of the discharge tube not shown in the drawing may be provided with a luminescent layer, e.g.

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Mg-tungstate, Zn-Be-silicate or with any other luminescent material or any mixture of luminescent materials.

What is claimed by Letters Patent is:

1. The process of preparing an electron-emissive material for electric-discharge devices, comprising thoroughly admixing the following constituents in the indicated molar ratios: one mole of  $\text{BaCeO}_3$ ,  $x$  mole  $\text{CeO}_2$  and  $x$  mole  $\text{BaF}_2$ , where  $x$  is from 0.01 to 1; then firing said admixture in an air atmosphere at from 1200 to 1400° C. for about two to three hours; and thereafter firing said admixture at from 1350 to 1400° C. in a hydrogen atmosphere for from two to three hours.

2. The process of preparing an electron-emissive material for electric-discharge devices, comprising thoroughly admixing the following constituents in the indicated molar ratios: one mole of  $\text{BaCeO}_3$ ,  $x$  mole  $\text{CeO}_2$  and  $x$  mole  $\text{BaF}_2$ , where  $x$  is from 0.1 to 0.3; then firing said admixture in an air atmosphere at from 1200 to 1400° C. for about two to three hours; and thereafter firing said admixture in a hydrogen atmosphere at more than 1000° C. for at least one-half hour and until a semi-conductive state is achieved.

3. The process of preparing an electron-emissive material for electric-discharge devices, comprising thoroughly admixing together the following constituents in the indicated molar ratios: one mole of  $\text{BaCeO}_3$ ,  $x$  mole  $\text{CeO}_2$  and  $x$  mole  $\text{BaF}_2$ , where  $x$  is from 0.1 to 0.3; then firing said admixture in an air atmosphere at from 1200 to 1400° C. for about two to three hours; and thereafter firing said admixture at from 1350 to 1400° C. in a hydrogen atmosphere for from two to three hours.

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4. The method of preparing an electron-emissive material for electric-discharge devices, comprising thoroughly admixing together the following constituents in the indicated molar ratios: two moles  $\text{BaCeO}_3$ ,  $x$  mole  $\text{BaCO}_3$  and  $x$  mole  $\text{CeF}_3$ , where  $x$  is from 0.01 to 1; then firing said admixture in an air atmosphere at from 1200 to 1400° C. for about two to three hours; and thereafter firing said admixture at from 1350 to 1400° C. in a hydrogen atmosphere for from two to three hours.

5. The method of preparing an electron-emissive material for electric-discharge devices, comprising thoroughly admixing together the following constituents in the indicated molar ratios: two moles  $\text{BaCeO}_3$ ,  $x$  mole  $\text{BaCO}_3$  and  $x$  mole  $\text{CeF}_3$ , where  $x$  is from 0.1 to 0.3; then firing said admixture in an air atmosphere at from 1200 to 1400° C. for about two to three hours; and thereafter firing said admixture at from 1350 to 1400° C. in a hydrogen atmosphere for from two to three hours.

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