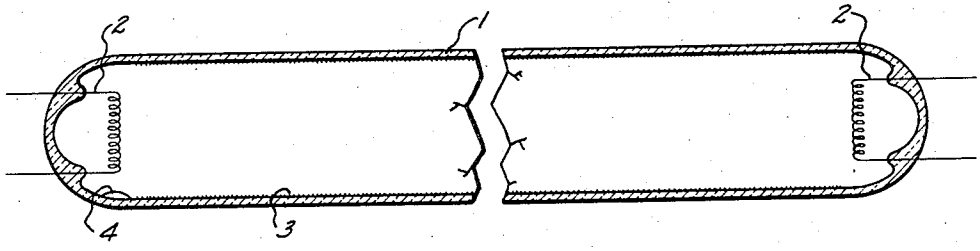
Aug. 6, 1940. M. SERVIGNE 2,210,780

ELECTRIC DISCHARGE TUBE

Filed Dec. 1, 1936



Inventor:
Marcel Servigne,
by Harry E. Dunham
His Attorney.

Patented Aug. 6, 1940 2,210,780

UNITED STATES PATENT OFFICE

2,210,780

ELECTRIC DISCHARGE TUBE

Marcel Servigne, Paris, France, assignor to Societe Pour l'Etude & l'Exploitation des Matieres Luminescentes, Paris, France

Application December 1, 1936, Serial No. 113,726
In Great Britain November 18, 1936

9 Claims. (Cl. 176—122)

It is known that the luminescent substances employed in electric discharge tubes generally have a base of fluorescent compounds, such as tungstates, molybdates, silicates or sulphides. These materials may contain the usual proportions (generally less than one hundredth part) of luminogenic common heavy metals, such as copper, manganese, bismuth and so forth. In all cases, each substance of the base possesses an emission comprising one or more characteristic maxima in well-defined regions of the visible spectrum. The possible addition of luminogens does not generally determine the appearance, in the spectrum composition of the resultant emission, of another maximum comparable in intensity with the first and consequently adapted to substantially influence the eye. For example, calcium tungstate, under the excitation of ultraviolet light, gives an emission with a pronounced maximum of intensity in the blue, practically irrespective of the common heavy metal utilised with it as luminogen.

It has been found, however, according to the present invention that if, instead of or in addition to a common heavy metal, there is employed as luminogen a metal of the rare earths, the emission of which is different from the fundamental emission of the basic body, the resulting luminescent material posssesses the unexpected property of comprising another maximum, due to the luminogen, of intensity comparable with the maxima of the basic body. It follows that if the luminescent material comprising these rare metals is placed in a gas-filled electric discharge tube under the usual conditions for use in lighting, it gives for the case of samarium added to tungstate a light varying according to the proportions from violet (red of samarium + blue) to bright red, whereas pure tungstate or tungstate to which have been added common heavy metals always retains in its emission the dominant bright blue shade which is characteristic of it.

According to the invention, the preceding properties are utilized in gaseous electric discharge tubes by effecting the discharge in direct contact with a solid solution of rare earths in fluorescent salts of tungstic or molybdic acid (for example, solid solutions of calcium tungstate in samarium).

The luminescent material according to the present invention may be prepared by calcination. For example, there may be used calcium tungstate, so-called "chemically pure for analyses," with which is incorporated in the usual manner, by calcination, the samarium, the nitrate of which in solution has served for moistening the tungstate.

The proportion of samarium may vary from 2 parts per 100 parts of tungstate to 1 part per 1000, which of course will produce a corresponding variation of the intensity of the red of the emission, and accordingly a variation in the inverse direction of the relative intensity of the blue of the tungstate. Consequently, by varying the proportion of samarium it will be possible to obtain a spectrum composition comprising a red maximum and a blue maximum, the relative values of which may be chosen so as to furnish a substantially white light by the addition of a suitable quantity of a substance having a green luminescence, zinc silicate for example.

But it has been stated that if, in place of calcining the mixture at about 800° C. as usual, complete fusion of the mass is effected, the emission of the rare earth is greatly increased. For example, a bright red color is obtained with 1% of samarium in calcium tungstate by complete fusion, whereas simple calcination at about 800° C. for a quarter of an hour, under the same conditions, gives a material having a luminescence which is simply violet (red + blue). It follows that the quantity of rare metal necessary for the production of a given colour is diminished by employing total fusion.

Moreover, the present invention provides another means of varying the color emitted by a substance of given composition of rare metal while the tube is actually operating; this means utilizes the sensitivity to heat of the different parts of the emission referred to hereinbefore. It has been ascertained, according to the present invention, that, in the same substance, the characteristic emission of the rare earth remains substantially constant under the influence of heat, in spite of the weakening of the characteristic emission of the base substance; this is a property entirely characteristic of the rare earths. Now it is known that the temperature of the wall of the tube, and consequently of the luminescent substance according to the present invention, varies according to the electric conditions to which the tube is subjected; thus, by varying the current density in the tube, there is produced a corresponding variation of the relative value of the intensity of the characteristic luminescent emission of the rare earths in respect to that of the base substances. Thus, in the case of a solid solution of samarium in tungstate, when the tube is fed with heavy current in-

tensities, the temperature becomes such that the blue emission of the tungstate weakens considerably, resulting in a reddening of the color of the visible luminescence. It will be seen that this rise in temperature during the operation of the tube has actually produced a relative effect analogous to that which, in the absence of the liberated heat, would result from an increase in the proportion of samarium in the tungstate. There is thus found a means of utilising a form of energy, the heat, produced in the tubes, which energy was normally harmful and in any case lost, in the case of all the substances known heretofore.

If erbium is employed instead of samarium, a yellow green will be obtained for that body instead of the red and its use with tungstates or molybdates will provide superposition effects analogous to those explained hereinbefore by way of example with samarium. The same will be the case for dysprosium, the characteristic luminescence of which is yellow, for gadolinium having an ultraviolet luminescence, and so forth.

Suitable quantities of fluxes may be added, that is to say, alkali-metal salts such as sodium chloride or sodium borate. Furthermore, if the final substances are alterable, they will be stabilised by the addition of the bodies specified in my co-pending patent application No. 113,725 filed on December 1, 1936, now Patent No. 2,179,-134, that is, tricalcium phosphate and/or calcium borate.

By way of example, the following composition will be indicated, which gives a substantially white light in a mercury vapour tube:

	Parts
Calcium molybdate	50
Samarium oxide	1/20
Sodium borate	5
Tricalcium orthophosphate	50

For the production of white light, the interest of the use of samarium to which the present invention specially relates, is that it enables a sufficient proportion of red to be obtained in a given mixture with tubes fed with a heavy current intensity and hence having a very high luminous efficiency.

The discharge tubes according to the present invention operate as those heretofore usual, from a pressure of the order of 1 millimetre mercury up to the high pressure of tens of atmospheres. But it has been recognized, according to the present invention, that one could also employ these tubes under low pressures smaller than 1/10 millimetre mercury; for example, with an atmosphere of xenon at the pressure of 1/100 millimetre mercury, particularly intense luminesence is obtained.

The figure of the accompanying drawing shows, by way of example, a schematic view of an electric discharge tube embodying the present invention.

In this figure, there is shown a mercury vapor discharge tube 1, the mercury being introduced in the form of a drop 4. Tube 1 is provided at its ends with electrodes 2. A luminescent layer 3 is disposed on the internal wall of the tube by any known means.

What I claim is:

1. A mercury vapor electric discharge lamp with luminous discharge comprising a container and a luminescent substance within said container, said luminescent substance comprising a solid solution of a rare earth in a fluorescent salt of an acid selected from the group consisting of tungstic and molybdic acids, the percentage of rare earth of the solid solution lying between 0.1 and 2 per cent and being sufficient to give rise during the operation of the lamp to a light comprising the combination of a maximum of emission corresponding to the solvent and of another maximum at least of the same order of magnitude as the first one, corresponding to the presence of the rare earth in the solid solution.

2. A mercury vapor electric discharge lamp according to claim 1, in which the solid solution is mixed with a material consisting of at least one of the materials selected from the group consisting of tricalcium phosphate and calcium borate.

3. A mercury vapor electric discharge lamp with luminous discharge comprising a container and a luminescent substance within said container, said luminescent substance comprising a solid solution of samarium in fluorescent calcium tungstate, the percentage of samarium of the solid solution lying between 0.1 and 2 per cent and being sufficient to give rise during the operation of the lamp to a light comprising the combination of a maximum of emission corresponding to the calcium tungstate and of another maximum at least of the same order of magnitude as the first one, corresponding to the presence of the samarium in the solid solution.

4. A mercury vapor electric discharge lamp with luminous discharge comprising a container and a luminescent substance within said container, said luminescent substance comprising a solid solution of rare earth in a fluorescent salt of an acid selected from the group consisting of tungstic and molybdic acids, said solid solution being obtained by total fusion of a mixture of its constituents and the percentage of rare earth of the solid solution lying between 0.1 and 2 per cent and being sufficient to give rise during the operation of the lamp to a light comprising the combination of a maximum of emission corresponding to the solvent and of another maximum at least of the same order of magnitude as the first one, corresponding to the presence of the rare earth in the solid solution.

5. A mercury vapor electric discharge lamp with luminous discharge comprising a container and within said container a solid solution of samarium in fluorescent calcium tungstate, said solid solution being obtained by total fusion of a mixture of its constituents, and a quantity of zinc silicate mixed with said solid solution, the quantity of samarium of the solid solution being such that the lamp emits a substantially white light.

6. A mercury vapor electric discharge lamp with luminous discharge comprising a container and within said container a solid solution of a rare earth in a fluorescent salt of an acid selected from the group consisting of tungstic and molybdic acids, said solution being obtained by total fusion of a mixture of its constituents and the quantity of rare earth of the solid solution being such as to give rise to a light appearing to the eye as substantially consisting of the emission due to the present of the rare earth.

7. A mercury vapor electric discharge lamp with luminous discharge comprising a container and a luminescent substance within said container, said luminescent substance comprising a solid solution of samarium in fluorescent calcium tungstate and a quantity of zinc silicate mixed with said solid solution, the thermal action on said solid solution of the electric current through

the lamp being such that the lamp emits a substantially white light, and the percentage of samarium of the solid solution lying between 0.1 and 2 per cent and being sufficient to give rise during the operation of the lamp to a light comprising the combination of a maximum of emission corresponding to the calcium tungstate and to another maximum of the same order of magnitude as the first one, corresponding to the presence of the samarium in the solid solution, but being insufficient to produce the desired effect under the working conditions for which said thermal action is practically negligible.

8. A mercury vapor electric discharge lamp with luminous discharge comprising a container and a luminescent substance within said container, said luminescent substance comprising a solid solution of samarium in fluorescent calcium tungstate, the thermal action on said solid solution of the electric current through the lamp being adapted to the obtaining of a light appearing to the eye as substantially consisting of the emission due to the presence of the samarium in the solid solution, and the percentage of samarium of the solid solution lying between 0.1 and 2 per cent and being sufficient to give rise during the operation of the lamp to a light comprising the combination of a maximum of emission corresponding to the calcium tungstate and of another maximum at least of the same order of magnitude as the first one, corresponding to the presence of the samarium in the solid solution, but being insufficient to produce the desired effect under the working conditions for which said thermal action is practically negligible.

9. The process of varying the color of the light emitted by a mercury vapor electric discharge lamp according to claim 1 by varying, within the working limits of the lamp, the current density in the lamp and thereby, the thermal action of the discharge on the solid solution.

MARCEL SERVIGNE.