United States Patent [19]

Blasse et al.

[11] **3,748,516**

[45] **July 24, 1973**

[54] **LOW-PRESSURE MERCURY VAPOUR DISCHARGE LAMP**

[75] Inventors: **George Blasse; Jaap De Vries,** both of Emmasingel, Eindhoven, Netherlands

[73] Assignee: **U.S. Philips Corporation,** New York, N.Y.

[22] Filed: **Feb. 16, 1971**

[21] Appl. No.: **115,787**

Related U.S. Application Data

[62] Division of Ser. No. 834,285, June 18, 1969, Pat. No. 3,586,637.

[30] **Foreign Application Priority Data**

June 22, 1968 Netherlands 6808846

[52] **U.S. Cl.** **313/109**

[51] **Int. Cl.** **H01j 1/63**

[58] **Field of Search** ..... 313/109; 252/301.4 P, 301.4 R

[56] **References Cited**

UNITED STATES PATENTS

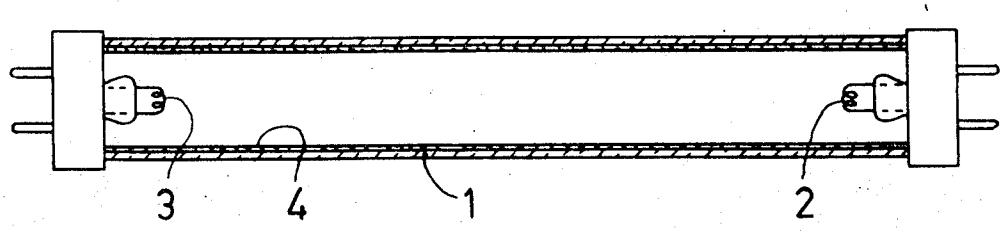
3,205,394	9/1965	Ray	313/109
3,516,940	6/1970	Lagos	252/301.4 P
3,522,191	7/1970	Turner et al.	252/301.4 R

Primary Examiner—Roy Lake
Assistant Examiner—James B. Mullins
Attorney—Frank R. Trifari

[57] **ABSTRACT**

Luminescent material for a low-pressure mercury vapor lamp consisting essentially of a europium activated strontium or barium boro-phosphate.

4 Claims, 3 Drawing Figures



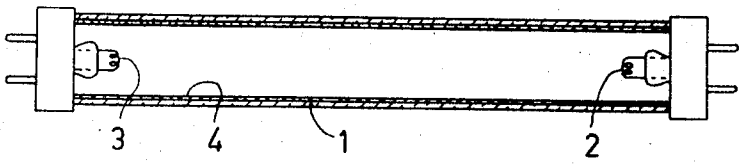


fig.1

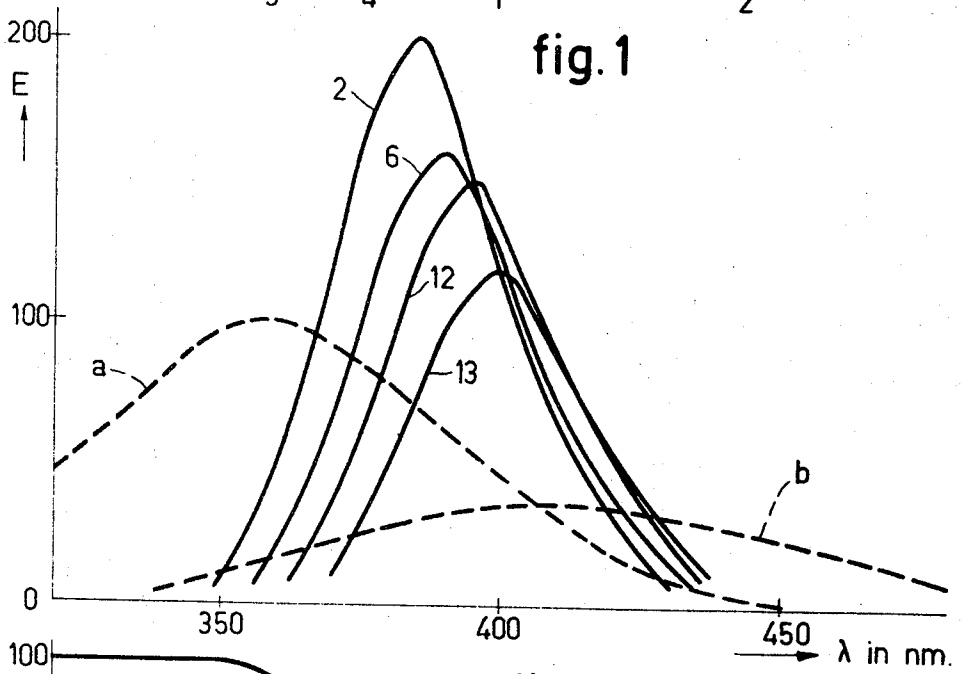


fig.2

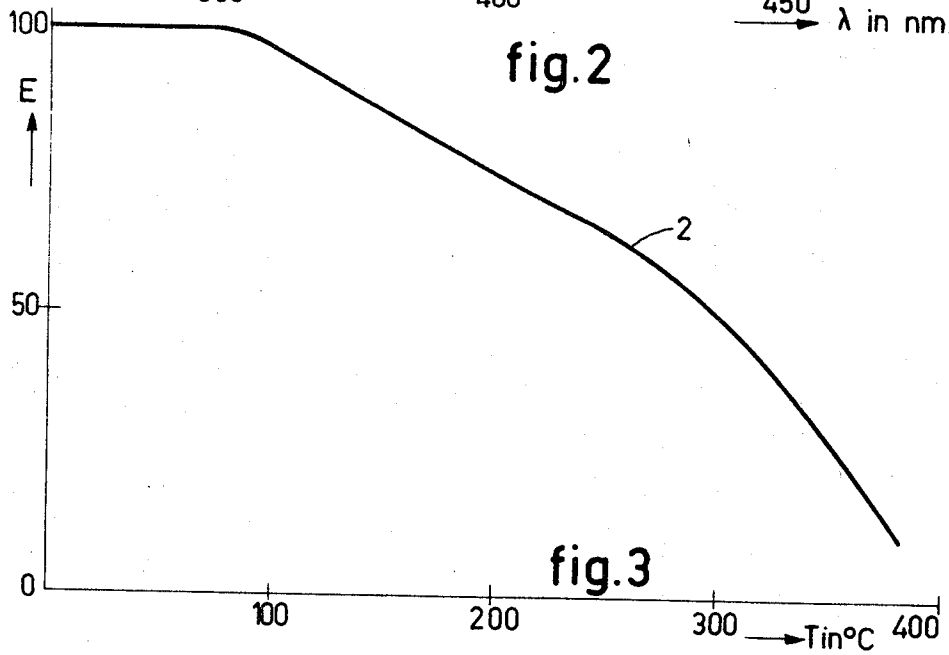


fig.3

LOW-PRESSURE MERCURY VAPOUR DISCHARGE LAMP

This application is a division of copending U.S. Pat. application Ser. No. 834,285, filed June 18, 1969 and now U.S. Pat. No. 3,586,637.

The invention relates to a novel luminescent material and to a low-pressure mercury vapor lamp employing such a material.

In many photochemical document-copying systems a document is copied by irradiating the master and directing the radiation which has been reflected or transmitted to a piece of paper which is sensitive to this radiation and contains substances which can be decomposed by the radiation so that a copy of the master document is obtained possibly after further treatment, for example, fixing.

For efficient use of the reproduction papers it is of course desirable to have a radiation source which emits a strong radiation at those wavelengths to which the paper is most sensitive.

A requirement generally imposed on the reproduction papers to be used is that the substances which are sensitive to radiation are converted as little as possibly by normal daylight. This of course facilitates working with these papers and also imposes few requirements on the storage thereof. Since normal daylight contains comparatively little ultraviolet radiation, the best combination is apparently a paper which has a maximum sensitivity below 400 nm. and a radiation source which emits a strong ultraviolet radiation.

As already stated above, the master to be copied must transmit or reflect the radiation. It has been found that many documents are made from paper which transmits and/or reflects ultraviolet radiation comparatively poorly. In view of the contradictory requirements for document-copying machines, a compromise must therefore be made: it is therefore preferred to use light-sensitive papers the maximum sensitivity of which lies between 380 and 440 nm and a radiation source having a maximum of the emitted radiation between these two values.

Document-copying machines generally use as radiation sources mercury vapour discharge lamps including a luminescent layer provided on a support, which layer converts a great part of the ultraviolet radiation produced in the mercury vapour discharge into radiation of longer wavelength. Thus, as described above, the maximum emitted radiation energy must preferably be in the wavelength range between 380 and 440 nm. This is, for example, the case with the very frequently used substance, calcium tungstate. The conversion efficiency of the ultraviolet radiation of the mercury vapour discharge into radiation between 380 and 440 nm. is however, comparatively small for this substance, because the emission spectrum is very wide and hence much radiation energy is emitted at wavelength outside this range. In addition the absorption spectrum of most light-sensitive papers is considerably narrower than this range. As a result of these two causes only a comparatively small part of the total radiation energy emitted by the calcium tungstate is efficiently used by the sensitive paper.

A further luminescent substance, which is very frequently used, is a lead-activated silicate of strontium, barium and magnesium. The emission spectrum of this substance is not very wide when excited by the ultraviolet radiation of a mercury vapour discharge and hence

is more suitable for adaptation to the absorption spectrum of a radiation-sensitive paper; the maximum emission of this substance lies, however, at 355 nm. and is therefore less suitable to be transmitted or reflected by the paper of most documents. In spite of this fact, the substance is very frequently used on account of the narrow emission band and the strong radiation.

A low-pressure mercury vapour discharge lamp according to the invention includes a luminescent material provided on a support and is characterized in that this luminescent material is an alkaline earth borate-phosphate activated by bivalent europium and having the following composition.

$$(Ba, Sr)_{1-x-p}Ca_xEu_p\ BPO_5$$

in which $0 \leq x \leq 0.5$
and $0.003 \leq p \leq 0.15$.

A luminescent material which is represented by the above formula can be excited satisfactorily by ultraviolet radiation which is emitted by a low-pressure mercury vapour discharge lamp and the material then shows an emission spectrum in which the greater part of the luminescent energy is radiated between 380 nm. and 440 nm. Since the conversion efficiency is also very high, namely considerably higher than that of calcium tungstate and also higher than that of the above-mentioned silicate, a lamp according to the invention is more suitable for use in document-copying apparatus in combination with available radiation-sensitive types of paper having a maximum absorption within this range, because all requirements as set above are now simultaneously satisfied. In addition, it has been found that the substances according to the invention have a good temperature dependence, that is to say, their conversion efficiency decreases only slightly as the temperature increases. They are thus very suitable for use in high-power, low-pressure mercury vapour discharge lamps, whose wall temperature assumes a high value during operation.

As is evident from the above-given formula, a luminescent material according to the invention consists of a bivalent europium-activated borate-phosphate of barium and/or strontium, wherein the barium and/or strontium may be partly replaced by calcium. The fundamental lattices of the borate-phosphates of the alkaline earth metals barium, strontium and calcium are isomorphous.

The pure barium borate-phosphate activated by bivalent europium is preferred because this substance has the highest light output. This substance has its maximum emission at a wavelength of approximately 385 nm. The pure strontium borate-phosphate activated by bivalent europium has its maximum emission at a wavelength of approximately 390 nm. The barium-strontium borate-phosphates according to the invention have their maximum emission at wavelength between the above-mentioned values and a light output which is approximately equal to that of the pure strontium borate-phosphate.

Tests have shown that the pure calcium borate-phosphate when activated by bivalent europium, is no usable luminescent substance due to its small light output. The emission spectrum has, however, a maximum at approximately 405 nm. and by partial replacement of barium and/or strontium in the barium strontium borate-phosphates by calcium, luminescent substances can be obtained whose location of the maximum emis-

sion in the spectrum is shifted to longer wavelengths. The calcium content x must, however, remain within the above-given limits because otherwise luminescent substances are obtained which are not usable for practice.

The amount of bivalent europium may be varied between the above-mentioned limits, but is preferably chosen to be between 0.005 and 0.05. In fact, the highest radiation efficiency is found in this range.

In addition to the above-mentioned advantages of the materials according to the present invention it is to be noted that the substances are only slightly affected by oxidation. This is of great importance in the manufacture of the mercury vapour discharge lamps, because they are then often exposed for a short period to a heat treatment in air at a fairly high temperature, for example, 600°C. Such a heat treatment is necessary, for example, when an organic binder is used which is to be removed later on by heat treatment.

Some embodiments of the present invention will now be described with reference to one Table, one Example and one drawing.

TABLE

Example	Formula	Composition firing mixture in grams						Location maximum emission (nm.)	Rel. light output
		$BaCO_3$	$SrCO_3$	$CaCO_3$	$BuBO_3$	H_3BO_3	$(NH_4)_2HPO_4$		
1	$Ba_{0.995}Eu_{0.005}BPO_5$	1.970			0.009	0.750	1.320	385	80
2	$Ba_{0.99}Eu_{0.01}BPO_5$	1.960			0.016	0.750	1.320	385	105
3	$Ba_{0.98}Eu_{0.02}BPO_5$	1.940			0.036	0.750	1.320	385	125
4	$Ba_{0.95}Eu_{0.05}BPO_5$	1.880			0.089	0.750	1.320	385	116
5	$Ba_{0.9}Eu_{0.1}BPO_5$	1.782			0.178	0.750	1.320	385	92
6	$Sr_{0.99}Eu_{0.01}BPO_5$		1.460		0.018	0.750	1.320	390	85
7	$Ca_{0.99}Eu_{0.01}BPO_5$			0.990	0.018	0.750	1.320	405	20
8	$Ba_{0.6}Sr_{0.19}Eu_{0.01}BPO_5$	1.585	0.280		0.018	0.750	1.320	385	85
9	$Ba_{0.5}Sr_{0.49}Eu_{0.01}BPO_5$	0.990	0.721		0.018	0.750	1.320	388	80
10	$Ba_{0.2}Sr_{0.79}Eu_{0.01}BPO_5$	0.396	1.160		0.016	0.750	1.320	390	85
11	$Ba_{0.7}Ca_{0.29}Eu_{0.01}BPO_5$	1.385		0.290	0.018	0.750	1.320	390	90
12	$Ba_{0.4}Sr_{0.3}Ca_{0.29}Eu_{0.01}BPO_5$	0.792	0.441	0.290	0.018	0.750	1.320	395	80
13	$Sr_{0.5}Ca_{0.49}Eu_{0.01}BPO_5$		0.755	0.490	0.018	0.750	1.320	400	65

EXAMPLE

A mixture was made of the substances indicated in the Table in the quantities indicated for each Example in the Table. Since the boric acid partly evaporates during the reaction, an excess of H_3BO_3 of approximately 20 percent relative to the stoichiometric quantity is always used. The mixture was heated at a temperature between 400° and 600°C for approximately 4 hours. After cooling of the firing product obtained, it was ground and again heated at a temperature between 800° and 900°C for 4 hours. In both cases the heat treatment took place in a mixture of nitrogen and hydrogen. The ratio of nitrogen to hydrogen is then not critical, a ratio of, for example, 20 : 1 was found to be quite usable. The hydrogen serves for reducing the trivalent europium to bivalent europium. After cooling subsequent to the second heat treatment the reaction product obtained was ground and sieved, if necessary. The product was then ready for use.

The last two columns of the Table state the wavelengths of the maximum of the emission band (in nm) and the relative light-outputs in arbitrary units for the different substances.

All measurements were made using an exciting radiation having a wavelength of 254 nm.

In the drawing

FIG. 1 diagrammatically shows a low-pressure mercury vapour discharge lamp according to the invention;

FIG. 2 is a graphic representation of the radiation intensities of a few substances according to the invention, and of two known substances as a function of the wavelength;

FIG. 3 is a graphic representation of the variation of the radiation intensity of the substance of Example 2 of the Table with temperature.

FIG. 1 shows a low-pressure mercury vapour discharge lamp which includes an envelope **1**. Electrodes **2** and **3** between which the discharge takes place during operation of the lamp are provided at the ends of the lamp. The inner side of the envelope **1**, which is made of, for example, glass is coated with a luminescent layer **4** which contains a luminescent material according to the present invention. The luminescent material may be provided on the envelope **1** by bringing a suspension of the luminescent material and nitrocellulose in butyl acetate into contact with the inner side of the envelope, whereby a thin layer of the suspension is left on the envelope. The nitrocellulose serves as a temporary adhesive. Then the envelope is subjected to a thermal treatment by which the temporary adhesive is removed and a satisfactory adhesion of the luminescent layer is obtained.

The broken-line curve *a* in the graph of FIG. 2 shows the spectral energy distribution of the known lead-activated silicate of barium, strontium and magnesium, and the broken-line curve *b* shows the spectral energy distribution of the known calcium tungstate. These curves are shown for comparison both for the spectral distribution and for the intensity of the luminescent radiation. The maximum intensity of the curve *a* is fixed at 100. The curves **2, 6, 12** and **13** relate to the materials of Example 2, 6, 12 and 13 of the Table. As is clearly evident from the drawing, the luminescent materials according to the invention have higher peak values and a narrower emission range as compared with the known silicate and the known tungstate, while they have a more favourable location of the maximum emission in the spectrum as compared with the known silicate.

The curve **2** in the graph of FIG. 3 shows the temperature dependence of the radiation intensity of the material of Example 2. The temperature is plotted in °C on the abscissa. The maximum intensity is fixed at 100. The Figure shows that the borate-phosphates according to the invention have a very good temperature dependence. The barium borate-phosphate still shows an intensity of the luminescent radiation at approximately 300°C which is equal to half the maximum value. It may be noted for comparison that already at 75°C the intensity of the known calcium tungstate has decreased to half the value at room temperature.

It is still to be noted that the luminescent substances according to the invention may also be excited by elec-

trons. In that case they have the same emission as when excited by ultraviolet radiation.

What we claim is:

1. In a low-pressure mercury vapor discharge lamp, a support and a layer of a luminescent material provided on said support, said luminescent material consisting essentially of an alkaline earth boro-phosphate activated by bivalent europium and having the formula $(BaSr)_{1-x-p}Ca_xEu_pBPO_5$ wherein $0 \leq x \leq 0.5$ and $0.003 \leq p \leq 0.15$.

2. The low-pressure mercury vapor discharge lamp of claim 1 wherein the alkaline earth boro-phosphate activated by bivalent europium has the formula $Ba_{1-p}Eu_pBPO_5$ wherein $0.003 \leq p \leq 0.15$.

3. The low-pressure mercury vapor discharge lamp of claim 1 wherein $0.005 \leq p \leq 0.05$.

4. The low-pressure mercury vapor discharge lamp of claim 2 wherein $0.005 \leq p \leq 0.05$.

* * * * *