PATENT SPECIFICATION

581,778

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PROVISIONAL SPECIFICATION

Improvements in Luminescent Materials

We, THE GENERAL ELECTRIC COMPANY LIMITED, of Magnet House, Kingsway, London, W.C.2, a British company, and ALFRED HAMILTON MCKEAG and PETER WHITTEN RANBY, both of Research Laboratories of the General Electric Company Limited, Wembley, Middlesex, both British subjects, do hereby declare the nature of this invention to be as follows:—

This invention relates to phosphorescent materials. For the purpose of the specification a luminescent material is to be deemed phosphorescent if, when it is used as the luminescent material in a fluorescent lamp operated on 50 cycle A.C., the flicker is appreciably less than if the luminescent material were one (e.g. magnesium tungstate) having no appreciable phosphorescence. This probably means that the period between the cessation of excitation and the instant when the phosphorescent light has become half of its initial value considerably exceeds 10^{-4} sec. The primary object of this invention is to provide phosphorescent materials that are excited by 2537 Å radiation and yield blue phosphorescent light when so excited; but the invention is not confined to material yielding blue phosphorescent light. The invention relates also to the manufacture of phosphorescent materials and to combinations (e.g. fluorescent lamps and cathode ray tubes) of phosphorescent materials with electrical means for exciting them to phosphorescence.

We have found that this object can be obtained by activating cadmium phosphate with lead, possibly associated with manganese. The manganese produces little or no phosphorescence by itself; when associated with lead it generally makes the phosphorescent light redder, but is apt to decrease the intensity or duration or both of the phosphorescence. The presence of a little fluorine may increase the phosphorescence.

According to the invention a material phosphorescing under excitation by 2537 Å radiation is prepared by heating (preferably to a temperature between 700° C. and 1000° C.) a substance containing as essential elements cadmium, phosphorus and oxygen (preferably in the form of the radical $-PO_4$), lead, and possibly manganese and fluorine or both, the said substance being either not a luminescent material or a luminescent material with luminescent properties other than those of the product of the heating. As already indicated it is probable that material according to the invention has a matrix with the lattice structure of some cadmium phosphate; but this is not yet fully established;.

Certain methods of preparing a phosphorescent material according to the invention will now be described, by way of example. The reagents mentioned should all be of the highest commercial purity.

Precipitated cadmium phosphate is prepared as follows: 956 gm. cadmium sulphate, 3 $CdSO_4 . 8H_2O$, is dissolved in 2500 ml. of hot distilled water to form solution A. 320 gm. diammonium hydrogen phosphate is dissolved in 1250 ml. of hot distilled water to form solution B. 10 ml. of solution A is added to solution B and *vice versa*; the solutions are filtered, the filtrates are mixed, the precipitate is separated, washed 6 times with hot distilled water, dried at 120° C. and ground.

Precipitated lead phosphate is prepared as follows: 189 gm. of lead acetate is dissolved in 500 ml. of hot distilled water to form solution A. 44 gm. of diammonium hydrogen phosphate is dissolved in 250 ml. of hot distilled water to form solution B. 10 ml. of solution A is added to solution B and *vice versa*; the solutions are filtered and the filtrates mixed. The precipitate is filtered off, washed 6 times with hot distilled water, dried at 160° C. and ground.

In the first example, 25 gm. of the cadmium phosphate is intimately mixed with 0.16 gm. of the lead phosphate. The mixture is heated for ½ hour at 800° C. in air; the product when cool is ground and heated again to 800° C. for ½ hour. The final product is ground, washed and sieved. Excitation by a low pressure mercury lamp with a quartz envelope (mainly by 2537 Å) gives a blue phosphorescence.

In the second example the process just described is modified only by the addition of 2.5 gm. cadmium fluoride to the mixture to be heated. The phosphorescence is

again blue, but somewhat stronger.

In the third example the process of the first example is modified only by the addition of 0.75 gm. manganese phosphate (prepared analogously to the cadmium and lead phosphates) to the mixture to be heated. The resulting phosphorescence is reddish.

It is not necessary that the lead and manganese (if present) should be introduced as phosphate. Thus the lead may be introduced as nitrate and the manganese as sulphate or chloride.

Dated the 6th day of August, 1943.
For the Applicants:
A. F. CORNOCK,
Chartered Patent Agent.

COMPLETE SPECIFICATION

Improvements in Luminescent Materials

We, THE GENERAL ELECTRIC COMPANY LIMITED, of Magnet House, Kingsway, London, W.C.2, a British company, and ALFRED HAMILTON MCKEAG and PETER WHITTEN RANBY, both of Research Laboratories of the General Electric Company Limited, Wembley, Middlesex, both British subjects, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to phosphorescent materials of the matrix-activator type. For the purpose of the specification a luminescent material is to be deemed phosphorescent if, when it is used as the luminescent material in a fluorescent lamp operated on 50 cycle A.C., the flicker is appreciably less than if the luminescent material were magnesium tungstate which has no appreciable phosphorescence. This probably means that the period between the cessation of excitation and the instant when the phosphorescent light has become half of its initial value considerably exceeds 10^{-4} sec. The primary object of this invention is to provide phosphorescent materials that are excited by 2537 Å radiation and yield blue phosphorescent light when so excited; but the invention is not confined to material yielding blue phosphorescent light. The invention relates also to the manufacture of phosphorescent materials and to combinations (e.g. fluorescent lamps) of phosphorescent materials with electrical means for exciting them to phosphorescence.

We have found that this object can be obtained by activating cadmium phosphate with lead, possibly associated with manganese. Manganese alone in cadmium phosphate produces little or no phosphorescence; when associated with lead it generally makes the phosphorescent light redder, but is apt to decrease the intensity or duration or both of the phosphorescence. Fluorine may also be included.

According to the invention a material phosphorescing under excitation by 2537 Å radiation is prepared by heating (preferably to a temperature between 700° C. and 1000° C.) a substance containing as essential elements cadmium, phosphorus and oxygen (the latter two elements preferably in the form of the radical $-PO_4$), lead, and possibly manganese and fluorine or both, the said substance being either not a luminescent material or a luminescent material with luminescent properties other than those of the product of the heating. As already indicated it is probable that material according to the invention has a matrix with the lattice structure of some cadmium phosphate; but this is not yet fully established. X-ray evidence of the structure of these compounds suggests that either cadmium orthophosphate $Cd_3(PO_4)_2$ or cadmium fluoro-phosphate $3Cd_3(PO_4)_2 . 1\,Cd\,F_2$ when activated by lead may show blue phosphorescence under excitation by radiation of 2537 Å, and to substantially the same degree. However such evidence is not conclusive because some orthophosphate is generally present in the fluorophosphate.

Certain methods of preparing a phosphorescent material according to the invention will now be described, by way of example. The reagents mentioned should all be of the highest commercial purity.

Precipitated cadmium phosphate is prepared as follows: 956 gm. cadmium sulphate, $3CdSO_4 . 8H_2O$, is dissolved in 2500 ml. of hot distilled water to form solution A. 320 gm. diammonium hydrogen phosphate is dissolved in 1250 ml. of hot distilled water to form solution B. 10 ml. of solution A is added to solution B and *vice versa*; the solutions are filtered, the filtrates are mixed, the precipitate is separated, washed 6 times with hot distilled water, dried at 120° C. and ground.

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In the second example, the process just described is modified only by the addition of 2.5 gm. cadmium fluoride to the mixture to be heated. The phosphorescence is again blue.

In the third example the process of the first example is modified only by the addition of 0.75 gm. manganese phosphate (prepared analogously to the cadmium and lead phosphates) to the mixture to be heated. The resulting phosphorescence is reddish.

It is not necessary that the lead and manganese (if present) should be introduced as phosphate. Thus the lead may be introduced as nitrate and the manganese as sulphate or chloride.

The materials described may be used in cathode ray tubes as they phosphoresce when excited by cathode rays. The phosphorescence is, however, not sufficiently strong for most purposes.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A method of preparing a material of the matrix-activator type phosphorescent under excitation by 2537 Å radiation which comprises heating to a suitable temperature a substance containing as essential elements cadmium, phosphorous, oxygen and lead, the said substance being either not a luminescent material or a luminescent material with luminescent properties other than those of the product of the heating.

2. A method according to claim 1, wherein said temperature is between 700° C. and 1000° C.

3. A method according to claim 1 or 2, wherein at least a substantial part of said phosphorus and oxygen are present in the form of the radical PO_4.

4. A method according to claims 1, 2 or 3, wherein said substance contains also the element manganese.

5. A method according to claims 1, 2, 3 or 4, wherein said substance contains also the element fluorine.

6. A method according to claim 1, conducted substantially according to one of the three methods hereinbefore described by way of example.

7. A phosphorescent material of the type set forth, when prepared according to the method claimed in any of claims 1 to 6.

8. A phosphorescent material of the type set forth excitable to phosphorescence by radiation of wave-length 2537 Å and whose essential elements are cadmium, phosphorus, oxygen and lead.

9. A phosphorescent material according to claim 8, containing also the element manganese.

10. A phosphorescent material according to claim 8 or 9 containing also the element fluorine.

Dated the 12th day of December, 1945.
For the Applicants:
A. F. CORNOCK,
Chartered Patent Agent.

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2. A method according to claim 1, wherein said temperature is between 700° C. and 1000° C.

3. A method according to claim 1 or 2, wherein at least a substantial part of said phosphorus and oxygen are present in the form of the radical PO_4.

4. A method according to claims 1, 2 or 3, wherein said substance contains also the element manganese.

5. A method according to claims 1, 2, 3 or 4, wherein said substance contains also the element fluorine.

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8. A phosphorescent material of the type set forth excitable to phosphorescence by radiation of wave-length 2537 Å and whose essential elements are cadmium, phosphorus, oxygen and lead.

9. A phosphorescent material according to claim 8, containing also the element manganese.

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