[Second Edition.]

# PATENT SPECIFICATION

578,272

*Application Date : June 17, 1942. No. 8309/42.*

*Complete Specification Left : June 7, 1943.*

*Complete Specification Accepted : June 21, 1946.*

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 luminescent materials ; its object is to provide luminescent materials that differ from previously known luminescent materials in their composition and are adapted for use in fluorescent lamps, cathode ray tube screens, X-ray screens, or for two or more of these uses. In general luminescent materials of different composition differ also in the colour or efficiency of their luminescence or in the excitation by which the luminescence is excited or in two or more of these properties ; but it may be observed that a material of a new composition might be useful even if it resembled very closely known materials in all these properties, thus, if tungsten became unobtainable, materials having the luminescent properties of the well known tungstates would become very important.

It is known that "calcium phosphate" can be rendered luminescent by suitable activators, and that among those suitable are tin and antimony. But in descriptions of these materials it is not usually stated definitely which of the various calcium phosphates is meant. We have found that calcium phosphate having the lattice structure (as indicated by X-ray analysis) of the pyrophosphate may be activated so as to provide very useful luminescent materials.

According to the invention the matrix of a luminescent material is calcium pyrophosphate. The term matrix implies the presence of an activator.

Calcium pyrophosphate activated by about ½% by weight of antimony gives highly saturated blue light when excited by the mercury line 2537 Å, by cathode rays of 6000 electron-volt energy, by X-rays of 1 Å wave-length, and by contact with a discharge through neon (which probably means the lines near 740 Å); it is little, if at all, excited by the 3650 Å mercury line. Activated by about ½% Sn it gives red light when excited by the said cathode rays ; it is not excited by the 2537 and 3650 Å lines. It may here be noted that the calcium phosphate material described in Patent Specification No. 512,154, when activated by tin, gives blue light ; it cannot therefore be the material concerned here. Activated by samarium calcium pyrophosphate gives brick red light under excitation by the said cathode- or X-rays, but is but little, if at all, luminescent under 2537 or 3650 Å. Activated by manganese it gives yellow light under the said cathode-rays, but little if any luminescence under 2537 or 3650 Å.

In the preparation of material according to the invention the proportion of $P_2O_5$ in the final product is somewhat critical and the best proportion depends somewhat on the exact treatment. Accordingly in place of giving precise instructions, we shall describe, by way of example, a method in which the desired result can be obtained with only a small amount of trial. The reagents should all be of high commercial purity, for example of AnalaR grade. AnalaR is a Registered Trade Mark.

500 ml. of AnalaR Phosphoric Acid are diluted to 1 litre with distilled water and 800 gm. of AnalaR calcium carbonate are added. When effervescence has ceased, the precipitate is separated, washed with distilled water, dried at 150° C. and ground. 25 gm. of the resulting phosphate are mixed with an aqueous solution of samarium chloride sufficient to give ½% of samarium in the mixture ; the paste is dried at 150° C. Different 5 gm. samples of the dried paste are mixed with sufficient ammonium phosphate $(NH_4)_2HPO_4$ to increase the $P_2O_5$ content by 2, 4, 6, 8% respectively. These samples together with one with no additive, are heated in air for about 1 hour at 1050—1100° C., ground, and then tested under suitable excitation, for example under cathode-ray excitation. That which gives

[*Price* 1*s*.]

the best luminescence is noted; large samples of the same composition are then made up and treated similarly.

If any activator other than samarium is used, it can be introduced at the same stage in an analogous manner.

Dated the 17th day of June, 1942.

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 luminescent materials; its object is to provide luminescent materials that differ from previously known luminescent materials in their composition and are adapted for use in fluorescent lamps, cathode ray tube screens, X-ray screens, or for two or more of these uses. In general luminescent materials of different composition differ also in the colour or efficiency of their luminescence or in the excitation by which the luminescence is excited or in two or more of these properties; but it may be observed that a material of a new composition might be useful even if it resembled very closely known materials in all these properties; thus if tungsten became unobtainable, materials having the luminescent properties of the well known tungstates would become very important. The invention relates also to electric discharge lamps and cathode ray tubes comprising luminescent materials adapted to be excited by the discharge in the lamp or by the cathode rays in the cathode ray tube.

It is known that "calcium phosphate" can be rendered luminescent by suitable activators, and that among those suitable are tin and antimony. But in descriptions of these materials it is not usually stated definitely which of the various calcium phosphates is meant. We have found that calcium phosphate having the lattice structure (as indicated by X-ray analysis) of the pyrophosphate may be activated so as to provide very useful luminescent materials.

According to the invention in a luminescent material that is an activated calcium phosphate, the lattice structure of the matrix is characteristic of calcium pyrophosphate and the activator is inorganic. The proviso that the activator is inorganic is inserted in view of the statement made in German Specification No. 652,609 that calcium phosphate can be activated by organic activators.

Calcium pyrophosphate activated by about 2% by weight of antimony alone gives blue light as highly saturated as that from calcium tungstate when excited by the mercury line 2537 Å, by cathode rays of 6000 electron-volt energy, by X-rays of 1 Å wave-length, and by contact with a discharge through neon (which probably means the lines near 740 Å); it is little, if at all, excited by the 3650 Å mercury line. Activated by about ½% Sn alone it gives red light when excited by the said cathode rays; it is not excited appreciably by the 2537 and 3650 Å lines. It may here be noted that the calcium phosphate material described in Patent Specification No. 512,154, when activated by tin, gives blue light; it cannot therefore be the material concerned here. Activated by ½% samarium alone, calcium pyrophosphate gives brick red light with considerable phosphorescence or afterglow under excitation by the said cathode or X-rays, but is but little if at all, luminescent under 2537 or 3650 Å. Activated by 1% manganese alone it gives yellow light under the said cathode-rays, but little if any luminescence under 2537 or 3650 Å.

Mixtures of these activators may be used, and especially a mixture of manganese with either antimony, tin, or samarium. The material then under excitation by 2537 Å gives a light which in general becomes redder and more deeply red the greater the proportion of manganese.

In the preparation of material according to the invention, the proportion of $P_2O_5$ in the final product is somewhat critical and the best proportion depends somewhat on the exact treatment. Accordingly in place of giving precise instructions, we shall describe, by way

of example, a method in which the desired result can be obtained with only a small amount of trial. The reagents sho. l all be of high commercial purity, for example of AnalaR grade. AnalaR is a Registered Trade Mark.

500 ml. of AnalaR Phosphoric Acid are diluted to 1 litre with distilled water and 800 gm. of AnalaR calcium carbonate are added. When effervescence has ceased, the precipitate of calcium phosphate is separated, washed with distilled water, dried at 150° C. and ground. 25 gm. of the precipitated phosphate are mixed with an aqueous solution of the activating metal, preferably as chloride, sufficient to give a suitable proportion of the metal in the mixture; the paste is dried at 150° C. Different 5 gm. samples of the dried paste are mixed with sufficient ammonium phosphate $(NH_4)_2 HPO_4$ to increase the $P_2O_5$ content by 2, 4, 6, 8% respectively. These samples, together with one with no ammonium phosphate, are heated in air for about 1 hour at 1050—1100° C. ground, and then tested under suitable excitation, for example under cathode-ray excitation. That which gives the best luminescence is noted; large samples of the same composition are then made up and treated similarly.

It will be observed that in this process the proportion of activator in the final mixture varies with the amount of ammonium phosphate added. But the proportion is not at all critical; thus, though 2% of antimony in the final material appears to be the optimum proportion, any proportion between 0.2% and 5% gives results not greatly inferior; it is only outside these limits that the luminescent efficiency of the material decreases notably. Accordingly the said "suitable proportion" may be identified with the optimum proportion if no ammonium phosphate were added.

The optimum amounts of the various activators singly are approximately those aforementioned in describing the effects of the activator. If manganese is added to another activator, proportions of the order of 5% of manganese are usually suitable.

But alternatives to this method are permissible. In another method, described by way of example, 10.7 gm. calcium phosphate, prepared as aforesaid, 1.5 gm. manganese phosphate and 0.24 gm. antimony trioxide are intimately mixed and heated in air at 1050° C. for 1 hour. The resulting material, excited by 2537 Å, yields pinkish light.

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 luminescent material that is an activated calcium phosphate, wherein the lattice structure of the matrix is characteristic of calcium pyrophosphate, and the activator is inorganic.

2. A luminescent material according to Claim 1 wherein the said activator is antimony or tin or samarium or a mixture of two or more of those elements.

3. A luminescent material according to Claim 1 wherein the said activator is a mixture with manganese of antimony or tin or samarium.

4. The method of preparing a luminescent material according to Claim 1, 2, or 3 wherein precipitated calcium phosphate is mixed with the activator or a compound thereof, wherein this mixture is mixed with ammonium phosphate, and wherein this second mixture is heated.

5. A method of preparing a luminescent material substantially as hereinbefore described by way of example.

6. A luminescent material prepared according to Claim 4 or 5.

7. An electric discharge lamp comprising a luminescent material according to Claim 1, 2, or 3 or prepared according to Claim 4, 5, 6 the said material being adapted to be excited by the discharge in the said lamp.

8. A cathode ray tube comprising luminescent material according to Claim 1, 2, or 3 or prepared according to Claim 4 or 5, the said material being adapted to be excited by the cathode rays in the said tube.

Dated the 2nd day of June, 1943.
For the Applicants,
A. F. CORNOCK,
Chartered Patent Agent.

Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 8229A.—1/1947.]

of example, a method in which the desired result can be obtained with only a small amount of trial. The reagents should all be of high commercial purity, for example of AnalaR grade. AnalaR is a Registered Trade Mark.

500 ml. of AnalaR Phosphoric Acid are diluted to 1 litre with distilled water and 800 gm. of AnalaR calcium carbonate are added. When effervescence has ceased, the precipitate of calcium phosphate is separated, washed with distilled water, dried at 150° C. and ground. 25 gm. of the precipitated phosphate are mixed with an aqueous solution of the activating metal, preferably as chloride, sufficient to give a suitable proportion of the metal in the mixture; the paste is dried at 150° C. Different 5 gm. samples of the dried paste are mixed with sufficient ammonium phosphate $(NH_4)_2HPO_4$ to increase the $P_2O_5$ content by 2, 4, 6, 8% respectively. These samples, together with one with no ammonium phosphate, are heated in air for about 1 hour at 1050—1100° C. ground, and then tested under suitable excitation, for example under cathode-ray excitation. That which gives the best luminescence is noted; large samples of the same composition are then made up and treated similarly.

It will be observed that in this process the proportion of activator in the final mixture varies with the amount of ammonium phosphate added. But the proportion is not at all critical; thus, though 2% of antimony in the final material appears to be the optimum proportion, any proportion between 0.2% and 5% gives results not greatly inferior; it is only outside these limits that the luminescent efficiency of the material decreases notably. Accordingly the said "suitable proportion" may be identified with the optimum proportion if no ammonium phosphate were added.

The optimum amounts of the various activators singly are approximately those aforementioned in describing the effects of the activator. If manganese is added to another activator, proportions of the order of 5% of manganese are usually suitable.

But alternatives to this method are permissible. In another method, described by way of example, 10.7 gm. calcium phosphate, prepared as aforesaid, 1.5 gm. manganese phosphate and 0.24 gm. antimony trioxide are intimately mixed and heated in air at 1050° C. for 1 hour. The resulting material, excited by 2537 Å, yields pinkish light.

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 luminescent material that is an activated calcium phosphate, wherein the lattice structure of the matrix is characteristic of calcium pyrophosphate, and the activator is inorganic.

2. A luminescent material according to Claim 1 wherein the said activator is antimony or tin or samarium or a mixture of two or more of those elements.

3. A luminescent material according to Claim 1 wherein the said activator is a mixture with manganese of antimony or tin or samarium.

4. The method of preparing a luminescent material according to Claim 1, 2, or 3 wherein precipitated calcium phosphate is mixed with the activator or a compound thereof, wherein this mixture is mixed with ammonium phosphate, and wherein this second mixture is heated.

5. A method of preparing a luminescent material substantially as hereinbefore described by way of example.

6. A luminescent material prepared according to Claim 4 or 5.

7. An electric discharge lamp comprising a luminescent material according to Claim 1, 2, or 3 or prepared according to Claim 4, 5, 6 the said material being adapted to be excited by the discharge in the said lamp.

8. A cathode ray tube comprising luminescent material according to Claim 1, 2, or 3 or prepared according to Claim 4 or 5, the said material being adapted to be excited by the cathode rays in the said tube.

Dated the 2nd day of June, 1943.
For the Applicants,
A. F. CORNOCK,
Chartered Patent Agent.

Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 8229A.—1/1947.]

