PATENT SPECIFICATION

Application Date: June 13, 1938. No. 17492/38.

516,870

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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, of Research Laboratories of the General Electric Company Limited, Wembley, Middlesex, a British subject, do hereby declare the nature of this invention to be as follows:

This invention relates to luminescent materials, that is to say, materials adapted to be excited to luminescence by a suitable agency, and more especially by electric discharges, for example an electric discharge emitting the mercury spectrum.

In co-pending Applications Nos. 10922/37 (Serial No. 495,706) and 1194/38 (Serial No. 495,706) there is described a new luminescent material (A) of which the essential characteristics are (1) that it contains cadmium and manganese and chlorine and phosphorus and oxygen, (2) that it has a certain lattice structure as revealed by X-ray analysis, (3) that under excitation by the mercury line of wave-length 2536 A.U. it emits warm luminescent light, that is to say, light whose colour departs from white in the direction of yellow or red and not in the direction of green or blue. In the complete specification based on those applications, it is explained why the material cannot be identified by the usual matrix-activator description.

We have now found another luminescent material of somewhat similar nature. It is prepared from materials containing cadmium and manganese and sodium and fluorine and phosphorus and oxygen. The lattice structure of the material appears to be much more complex than that of (A), and as yet can be defined only by a list of X-ray spacings. The luminescent light excited by radiation of wave-length 2536 A.U. is warm.

According to the invention a luminescent material is prepared from materials containing cadmium and manganese and sodium and fluorine and phosphorus and oxygen, (2) has a lattice structure giving rise to X-ray spacings set forth in Table I below, (3) under excitation by radiation of wave length 2536 A.U. emits warm luminescent light.

In Table I the symbols in columns (a) and (b) have the same significance as in Column II of the Table of provisional specification No. 10922/37 (Serial No. 495,706).

TABLE I.

(a)	(b)
8.64	1
6.30	1
5.74	2
4.07	1
3.778	3
3.728	3
3.346	5
3.243	3
3.096	8
2.925	5
2.885	6
2.826	5
2.751	2
2.601	4
2.546	5
2.459	5
2.369	1
2.229	2
2.192	1
2.155	2
2.040	1
1.967	3
1.906	1
1.872	5
1.851	2
1.822	4
1.809	2
1.770	1
1.747	4
1.725	4
1.686	2
1.625	1
1.586	3
1.557	3
1.541	1
1.533	1
1.507	1
1.486	1
1.470	1
1.452	2
1.430	1
1.421	1
1.38[illegible]	2
1.364	2
1.344	1
1.329	2
1.312	1
1.290	1
1.288	1
1.231	2

[Price 1/-]

One method of preparing material according to the invention will now be described by way of example.

478 gms. of cadmium sulphate (Analar grade) are dissolved in 1500 ml. of distilled water (Analar is a registered trade mark). 160 gms. of diammonium hydrogen phosphate (Analar grade) are dissolved in 1000 ml. of distilled water. The two solutions are heated to boiling. 10 ml. of the second solution are added to the first, and the precipitate produced is filtered off and discarded. The remainder of the second solution is added to the first and the precipitate is filtered off and washed six times with hot distilled water. It is dried at 180° C. in air; it will be called precipitate A.

500 gms. of manganese chloride (Analar grade) are dissolved in 2 litres of boiling distilled water. 220 gms. of diammonium hydrogen phosphate (Analar grade) are dissolved in 2 litres of boiling distilled water. The two solutions are mixed; the precipitate formed is filtered off and, after washing six times with hot distilled water, is dried at 180° C. in air. It will be called precipitate B.

The following mixture is prepared:

100 gms. of Precipitate A.
10 gms. of Precipitate B.
20 gms. of Sodium fluoride.

The mixture is heated to between 850° C. and 875° C. in a tubular boat with the open end, which projects from the furnace, closed with a glass wool plug. Sintering takes place rapidly between these temperatures; when it is complete the mixture is withdrawn. Any coloured material is separated; the remaining white material is reground and heated at 800° C. for ½ hr. The coloured part may be reheated several times at 800° C., with regrinding between heatings, until it becomes white.

The white powder is washed with hot distilled water and dried at 180° C. It luminesces red under excitation by either of the mercury lines 2536 or 3650 A.U.

The statements made in the aforesaid complete specification about mixing the material according to that invention with other materials, and about the use of the material, apply equally to the material according to the present invention, except possibly in respect of numerical values given for efficiencies and preferred current densities.

Dated the 13th day of June, 1938.
NORMAN R. CAMPBELL,
For the Applicants.

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, of Research Laboratories of the General Electric Company Limited, Wembley, Middlesex, a British subject, 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, to the manufacture of such materials, and to combinations of them with means for exciting them to luminescence.

In Patent Specification No. 495,706 there is described a new luminescent material (M) which contains all of the elements cadmium and manganese and chlorine and phosphorus and oxygen, and is prepared by a process which produces in the finished product a certain crystal structure, and is such that the finished product will emit, under excitation by the mercury line of wave-length 2536 A.U (which is now more usually said to be 2537 A.U), warm luminescent light, that is to say, light whose colour departs from white in the direction of yellow or red and not in the direction of green or blue. In the said specification it is explained why the material cannot be identified by the usual matrix-activator description.

We have now found another luminescent material of somewhat similar nature. It contains all of the elements cadmium and manganese and sodium and fluorine and phosphorus and oxygen. The luminescent light excited by radiation of wave-length 2537 A.U is warm. The lattice structure of the material appears to be much more complex than that of (M) and as yet can be defined only by a list of X-ray spacings. It has not been possible so far to relate these spacings to a crystal lattice, as was done for material (M). Accordingly, as those skilled in the art will understand, it is not possible to be sure that all the spacings that have been observed are characteristic of the luminescent material itself and that some of them are not characteristic of inert material produced with the luminescent material in the course of its manufacture; but the usual precautions of the art have been taken to ensure this result. However, in view of this inevitable uncer-

tainty, we desire to point out that hereinafter the crystal structure is said to be defined by the spacings. The term "defined" is, of course, to be interpreted according to present knowledge of X-ray analysis; two sets of spacings do not necessarily define two different crystal structures because one contains a small proportion of spacings that the other lacks, even when it can be shown that this small proportion of spacings is not really characteristic of the crystal structure of which the remainder are characteristic.

According to the invention a luminescent material contains all of the elements cadmium and manganese and sodium and fluorine and phosphorus and oxygen, and is prepared by a process which produces in the finished product a crystal structure defined by the X-ray spacings set forth in Table I below, and which is such that the finished product will emit under excitation by radiation of wave length 2537 A.U luminescent light whose colour is hereinbefore defined as warm.

In Table I the symbols in columns (a) and (b) have the same significance as in columns (1) and (2) of Table I on page 6 of the said specification No. 495,706.

TABLE I.

(a)	(b)	(a)	(b)
d/n	Intensity	d/n	Intensity
8.64	1	2.546	5
6.30	1	2.459	5
5.74	2	2.309	1
4.07	1	2.229	2
3.778	3	2.192	½
3.728	3	2.155	½
3.346	5	2.040	1
3.243	3	1.967	3
3.090	8	1.906	1
2.925	5	1.872	5
2.885	6	1.851	2
2.786	5	1.822	4
2.754	2	1.809	2
2.601	4	1.770	1
1.747	½	1.452	2
1.725	½	1.430	1
1.686	2	1.421	½
1.625	1	1.385	½
1.586	3	1.361	½
1.557	3	1.344	½
1.541	1	1.329	½
1.533	1	1.312	½
1.507	1	1.299	½
1.486	1	1.288	1
1.470	½	1.231	2

In every method by which we have actually prepared satisfactory material, a mixture is heated of which the components are cadmium phosphate, manganese phosphate, and sodium fluoride. One method of preparing it will now be described by way of example; it is, of course, in our opinion the best method known to us; and no reason is known why any other method should be used.

478 gm. of cadmium sulphate (AnalaR grade) is dissolved in 1.5 litres of distilled water (AnalaR is a registered trade mark). 160 gm. of diammonium hydrogen phosphate (AnalaR grade) is dissolved in 1 litre of distilled water. The two solutions are heated to boiling. 10 ml. of the second solution is added to the first, and the precipitate produced is filtered off and discarded. The remainder of the second solution is added to the first and the precipitate (some form of cadmium phosphate) is filtered off and washed six times with hot distilled water. It is dried at 180° C. in air; it will be called precipitate A.

500 gm. of manganese chloride (AnalaR grade) is dissolved in 2 litres of boiling distilled water. 220 gm. of diammonium hydrogen phosphate (AnalaR grade) is dissolved in 2 litres of boiling distilled water. The two solutions are mixed; the precipitate (some form of manganese phosphate) formed is filtered off and, after washing six times with hot distilled water, is dried at 180° C. in air. It will be called precipitate B.

The following mixture is prepared:

100 gms. of Precipitate A.
10 gms. of Precipitate B.
20 gms. of sodium fluoride, of the purity characteristic of the salt supplied by British Drug Houses Ltd.

The mixture is heated to between 850° C. and 875° C. in a tubular silica boat with the open end, which projects from the furnace, closed with a glass wool plug. Sintering takes place rapidly between these temperatures; when it is complete the mixture is withdrawn. Any coloured material is separated; the remaining white material is reground and heated at 800° C. for ½ hr. The coloured part may be reheated several times at 800° C. with regrinding between heatings, until it becomes white.

The white powder is washed with hot distilled water and dried at 180° C. It luminesces red under excitation by either of the mercury lines 2537 or 3650 A.U. but much more powerfully under 2537.

Like material (M), material according to the invention may be used in cathode-ray tubes, but its greatest utility is likely to be inside low-pressure mercury discharge lamps, and outside high-pressure mercury discharge lamps, especially with quartz envelopes. (The term "mercury"

does not exclude the presence, in addition to mercury, of other substances which may contribute appreciably to the light from the discharge). Like most luminescent materials, material according to the invention may be mixed in known manner with other luminescent materials, and in particular those giving under excitation by the same agency light of different colour, or with inert material.

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, which contains all of the elements cadmium and manganese and sodium and fluorine and phosphorus and oxygen, prepared by a process which produces in the finished product a crystal structure defined by the X-ray spacings set forth in Table I aforesaid, and which is such that the finished product will emit under excitation by radiation of wave-length 2537 A.U luminescent light whose colour is hereinbefore defined as warm.

2. The method of manufacturing a luminescent material according to Claim 1 which comprises the step of heating together a mixture of which the components are cadmium phosphate, manganese phosphate, and sodium fluoride.

3. A luminescent material prepared substantially as hereinbefore described by way of example.

4. Means for producing light comprising a combination of luminescent material with means adapted in operation to excite it to luminescence, wherein part at least of the said luminescent material (1) contains all of the elements cadmium and manganese and sodium and fluorine and phosphorus and oxygen, (2) has a crystal structure defined by the X-ray spacings set forth in Table I aforesaid, and (3) emits under excitation by radiation of wave-length 2537 A.U luminescent light whose colour is hereinbefore defined as warm.

5. Means for producing light comprising a combination of luminescent material with means adapted in operation to excite it to luminescence, wherein part at least of the said luminescent material has been manufactured according to Claim 2.

6. Means for producing light comprising a combination of luminescent material with means adapted in operation to excite it to luminescence, wherein part at least of the said luminescent material is luminescent material according to Claim 3.

7. Means according to Claim 4, 5, or 6 wherein the said exciting means is a low-pressure mercury-vapour discharge device and wherein the luminescent material is within the envelope of the said device.

Dated the 31st day of March, 1939.

NORMAN R. CAMPBELL,
For the Applicants.

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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, which contains all of the elements cadmium and manganese and sodium and fluorine and phosphorus and oxygen, prepared by a process which produces in the finished product a crystal structure defined by the X-ray spacings set forth in Table I aforesaid, and which is such that the finished product will emit under excitation by radiation of wave-length 2537 A.U luminescent light whose colour is hereinbefore defined as warm.

2. The method of manufacturing a luminescent material according to Claim 1 which comprises the step of heating together a mixture of which the components are cadmium phosphate, manganese phosphate, and sodium fluoride.

3. A luminescent material prepared substantially as hereinbefore described by way of example.

4. Means for producing light comprising a combination of luminescent material with means adapted in operation to excite it to luminescence, wherein part at least of the said luminescent material (1) contains all of the elements cadmium and manganese and sodium and fluorine and phosphorus and oxygen, (2) has a crystal structure defined by the X-ray spacings set forth in Table I aforesaid, and (3) emits under excitation by radiation of wave-length 2537 A.U luminescent light whose colour is hereinbefore defined as warm.

5. Means for producing light comprising a combination of luminescent material with means adapted in operation to excite it to luminescence, wherein part at least of the said luminescent material has been manufactured according to Claim 2.

6. Means for producing light comprising a combination of luminescent material with means adapted in operation to excite it to luminescence, wherein part at least of the said luminescent material is luminescent material according to Claim 3.

7. Means according to Claim 4, 5, or 6 wherein the said exciting means is a low-pressure mercury-vapour discharge device and wherein the luminescent material is within the envelope of the said device.

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