PATENT SPECIFICATION

610,025

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PROVISIONAL SPECIFICATION

Improvements in and relating to Luminescent Materials

We, THE GENERAL ELECTRIC COMPANY LIMITED, of Magnet House, Kingsway, London, W.C.2, a British Company, ALFRED HAMILTON MCKEAG, and PETER WHITTEN RANBY, both of Research Laboratories of the The General Electric Company Limited, Wembley, Middlesex, and 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.

The invention relates also to the manufacture of luminescent materials and to combinations (e.g. fluorescent lamps and cathode ray tubes) of luminescent materials with electrical means for exciting them to luminescence.

In Patent Specification No. 578,192, luminescent materials are described comprising a halo-phosphate wherein at least half of the bivalent metal atoms are calcium atoms or strontium atoms or a mixture of calcium and strontium atoms, wherein at least half of the halogen atoms are fluorine atoms or chlorine atoms or bromine atoms, or a mixture of atoms of two or more of fluorine, chlorine and bromine, which halo-phosphate is activated by an activator of which part at least is antimony. The material may contain also manganese. A halo-phosphate for the purpose of this invention means a substance having a lattice structure similar to that of apatite and comprising as essential constituents of the lattice one or more bivalent metals, the phosphate radical—(PO_4) and one or more halogens; the term "similar" implies that the difference of the structure from that of apatite is no greater than might be expected to result from either (*a*) the partial or complete substitution for the calcium or fluorine in apatite of another alkaline earth metal or another halogen respectively, or (*b*) the introduction of an activator. Halo-phosphates are generally supposed to be represented by $3M_3(PO_4)_2.1M^1L_2$, where M,M^1, which may be the same, are bivalent metals or mixtures of bivalent metals, and L is a halogen or mixture of halogens. Such luminescent materials can be prepared by heating to a temperature in the neighbourhood of 1000° C. (e.g. 1000—1150° C.) a substance containing as essential elements one or more halogens, antimony, manganese (if present), phosphorous, and oxygen, the said substance, usually a mixture of several chemical compounds in which the phosphorous and oxygen are present as the radical—PO_4, being either not a luminescent material or a luminescent material having luminescent properties other than those of the product of the heating.

In Patent Specification No. 580,363 there is described the replacement of antimony by lead or tin, or by both lead and tin, as a part at least of the activator.

It has now been discovered that good results can be obtained when the bivalent metal M,M^1 is barium, instead of strontium or calcium, and when the halogen is fluorine or chlorine, provided that the proportions of $BaCO_3$ and P_2O_5 are suitably chosen as will be explained later.

According to the present invention, therefore, an artificial luminescent

alkaline earth metals, one or more

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material comprises a halo-phosphate wherein at least half of the bivalent metal atoms are barium atoms, wherein at least half of the halogen atoms are fluorine atoms or chlorine atoms, or a mixture of atoms of fluorine and chlorine, and wherein there is included as activator antimony, tin or lead or a compound thereof or a mixture of two or more of antimony, tin and lead or compounds thereof.

Manganese may be provided as a secondary activator in order to change the colour of the fluorescence but the magnitude of the change produced is in this case substantially smaller than in the case of calcium halo-phosphates.

According to a feature of the present invention, a luminescent material comprising a halo-phosphate in which the bivalent metal M,M^1 is mainly barium is prepared by heating to a temperature. preferably in the neighbourhood of 1000° C., a substance containing as essential elements barium; chlorine or fluorine or both; one or more of the elements antimony, lead or tin; phosphorous; oxygen; and possibly manganese, 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.

Certain methods of preparing fluorescent materials according to this invention will be described by way of example. All of the reagents mentioned are preferably of the highest commercial purity, for example when obtainable they should be of the grade sold under the Registered Trade Mark AnalaR.

Barium fluoride may be prepared as follows: 244 grms. barium chloride ($BaCl_2.2H_2O$) (AnalaR) is dissolved in 1 litre of hot distilled water to form solution A. 100 grms. ammonium fluoride (AnalaR) is dissolved in 250 mls. of hot distilled water to form solution B. 10 mls. of solution A are added to solution B and 10 mls. of solution B are added to solution A. The resulting liquids are filtered and the filtrates are mixed. The precipitate is separated by filtration, washed six times with hot distilled water, dried at 160° C. and ground. Strontium fluoride may be prepared in an analogous manner.

Strontium chloride ($SrCl_2.6H_2O$) is prepared by dissolving strontium carbonate in the calculated quantity of dilute hydrochloric acid and crystallising from this liquor.

Barium phosphate may be prepared as follows: 1180 grms. Ba CO_3 (AnalaR) is mixed into a slurry with 1500 mls. of cold distilled water to form C. 255 mls. of phosphoric acid (AnalaR) is diluted to 500 mls. with cold distilled water and called solution D. C is added to solution D slowly and with constant stirring. When effervescence has ceased the liquid is filtered, the precipitate is dried at 160° C. and ground. Strontium phosphate may be prepared from strontium carbonate (AnalaR) in an analogous manner.

Antimony tri-oxide may be prepared as follows: 500 grms. antimony trichloride (AnalaR) is dissolved in the minimum amount of cold concentrated hydrochloric acid. Ammonia solution (AnalaR) (S.g.O. 880) is then slowly added with constant stirring until no further precipitation occurs. The precipitate is filtered off and washed six times in boiling distilled water, dried at 160° C. and ground. The resulting white powder may contain a little oxychloride of antimony.

Manganese phosphate may be prepared as follows: 396 gm. ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) (AnalaR) is dissolved in two litres of boiling distilled water to form solution E. 594 gm. manganese chloride (AnalaR) is dissolved in 3 litres of distilled water to form solution F. 10 mls. of solution E. is added to solution F, and 10 mls. of solution F to solution E; the resulting liquids are filtered and the filtrates mixed. The precipitate is separated by filtration, washed with boiling distilled water, and dried at 160° C. The dried product is ground.

EXAMPLE I.

If the material required is $3Ba_3(PO_4)_2.1\ BaF_2+3\%\ Sb+1.7\%\ Mn$, the substance to be heated may consist of a mixture of 66.3 grms. barium phosphate, 5.8 grms. barium fluoride, 2.4 grms. antimony tri-oxide and 2.6 grms. manganese phosphate. This mixture is furnaced in a silica boat closed by a glass wool plug at 1000° C. for ½ hour and allowed to cool. When cool the substance is ground and re-furnaced for a further ½ hour at the same temperature. If necessary a small amount of barium carbonate (AnalaR) or ammonium phosphate (AnalaR) may be added to the initial mixture to produce the optimum luminescent efficiency.

As has already been mentioned the proportions of $BaCO_3$ and P_2O_5 are critical for best results. It is frequently found that to achieve the optimum result it is necessary to adjust the relative proportions of these two constituents by the addition of one of them. The quantities of these substances to be added have been found to vary between about 0 and 2% $BaCO_3$ and between 0 and 4% P_2O_5; thus

in some cases a small quantity of $BaCO_3$ may be needed and in others a small quantity of P_2O_5 will be found to give best results.

The powder, after the second heat treatment, may be ground, washed and sieved to the required particle size. The powder shows a yellow fluorescence under U.V. light of 2537 Å.

Materials with different luminescent properties may be prepared by partially or completely replacing the barium fluoride by barium chloride and also by increasing or decreasing the percentage of manganese in the initial mixture. The luminescent colours and approximate brightnesses of some modified compositions are given in the following table:—

Composition	Percentage of Manganese 0	2	5	7.5
3 $Ba_3(PO_4)_2$.1 BaF_2 + 3% Sb	Bright yellow	Moderate yellow (more saturated)	Weak yellow	Weak yellow
3 $Ba_3(PO_4)_2$.1 BaFCl + 3% Sb	Moderate yellow (more saturated)	Weak yellow	Very weak yellow	——
3 $Ba_3(PO_4)_2$.1 $BaCl_2$ + 3% Sb	Weak yellow	Very weak yellow	——	——

EXAMPLE II.

If the material required is $3Ba_3(PO_4)_2$.1 BaF_2 + 5% Pb + 1.7% Mn, the substance to be heated may be a mixture of 66.3 grms. barium phosphate, 5.8 grms. barium fluoride, 3.3 grms. ammonium fluoride (AnalaR), 2.8 grms. manganese phosphate and 5.3 grms. lead nitrate (AnalaR). This mixture is furnaced in a silica boat closed by a glass wool plug at 950° C. for ½ hour. The product may then be ground, washed and sieved to the required particle size. As in the preceding example a small amount or barium carbonate or ammonium phosphate (usually from 0—2% $BaCO_3$ and 4—0% P_2O_5) is added to the initial mixture to produce the optimum luminescent efficiency. This powder shows a pinky-red fluorescence under U.V. light of 2537 Å.

EXAMPLE III.

The initial mixture of Example II is modified by the addition of 6.3 grms. stannous chloride (AnalaR) in place of the lead nitrate, and the method of preparation is otherwise the same as in Example II. This powder shows a yellow-green fluorescence.

EXAMPLE IV.

If the material required is $3Ba_3(PO_4)_2.\frac{1}{2}$ $BaF_2.\frac{1}{2}$ $BaCl_2$.3 $Sr_3(PO_4)_2.\frac{1}{2}$ $SrF_2.\frac{1}{2}$ $SrCl_2$ + 3% Sb + 1% Mn, the following mixture is prepared: 33.1 grms. barium phosphate, 25.8 grms. strontium phosphate, 1.5 grms. barium fluoride, 2.0 grms. barium chloride ($BaCl_2.2H_2O$) (AnalaR), 1.0 grms. strontium fluoride, 2.2 grms. strontium chloride ($SrCl_2.6H_2O$), 2.1 grms. antimony trioxide and 2.1 grms. manganese chloride ($MnCl_2.4H_2O$) (AnalaR). This mixture is ground and furnaced in a silica tube closed by a glass wool plug for half an hour at 1100° C. When cool the mixture is ground and re-furnaced. When again cool the mixture may be ground and washed with distilled water. When excited by short wave U.V. light of 2537 Å this powder shows a yellowy white luminescence.

If necessary in order to produce the best luminescence a small amount of barium carbonate or ammonium phosphate may be added before furnacing as in the previous examples.

EXAMPLE V.

If the material required is $3Ba_3(PO_4)_2.\frac{1}{2}$ $BaF_2.\frac{1}{2}$ $BaCl_2$.3 $Ca_3(PO_4)_2.\frac{1}{2}$ $CaF_2.\frac{1}{2}$ $CaCl_2$ + 3% Sb + 1% Mn, the following mixture is prepared: 33.1 grms. barium phosphate, 18.6 grms. calcium phosphate, 1.5 grms. barium fluoride, 2.0 grms. barium chloride ($BaCl_2.2H_2O$) (AnalaR), 0.7 grms. calcium fluoride, 1.3 grms, calcium chloride, 1.8 grams antimony trioxide and 1.8 grms. manganese chloride (AnalaR). The calcium phosphate and fluoride may be prepared as described in Patent Specification No. 578,192. The calcium chloride is dried, of AnalaR grade, and contains

about 27.5% of water. The remaining constituents may be prepared as described herein.

This mixture is ground and furnaced in a silica tube closed by a glass wool plug for half an hour at 1100° C. When cool the mixture is ground and re-furnaced. When again cool it may be ground and washed with distilled water. The powder shows a pale pink luminescence under short wave U.V. light 2537 Å. The content of $BaCO_3$ and P_2O_5 may, if necessary, be adjusted as already described.

Dated this 29th day of March, 1945.
A. F. CORNOCK,
Agent for the Applicants.

COMPLETE SPECIFICATION

Improvements in and relating to Luminescent Materials

We, THE GENERAL ELECTRIC COMPANY LIMITED, of Magnet House, Kingsway, London, W.C.2, a British Company, ALFRED HAMILTON MCKEAG, and PETER WHITTEN RANBY, both of Research Laboratories of the The General Electric Company Limited, Wembley, Middlesex, and 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 the manufacture of luminescent materials and to combinations (e.g. fluorescent lamps and cathode ray tubes) of luminescent materials with electrical means for exciting them to luminescence.

In Patent Specification No. 578,192, luminescent materials are described comprising a halo-phosphate wherein at least half of the bivalent metal atoms are calcium atoms or strontium atoms or a mixture of calcium and strontium atoms, wherein at least half of the halogen atoms are fluorine atoms or chlorine atoms or bromine atoms, or a mixture of atoms of two or more of fluorine, chlorine and bromine, which halo-phosphate is activated by an activator of which part at least is antimony. The material may contain also manganese. An activated halo-phosphate for the purpose of this invention means a substance having a lattice structure similar to that of apatite and comprising as essential constituents one or more bivalent metals, the phosphate radical—(PO_4), one or more halogens, and the activator; the term "similar" implies that the difference of the structure from that of apatite is no greater than might be expected to result from either (*a*) the partial or complete substitution for the calcium or fluorine in apatite of another alkaline earth metal or another halogen respectively, or (*b*) the introduction of the activator. Halo-phosphates are generally supposed to be represented by $3M_3(PO_4)_2.1M^1L_2$, where M,M^1, which may be the same, are bivalent metals or mixtures of bivalent metals, and L is a halogen or mixture of halogens. Such luminescent materials can be prepared by heating to a temperature in the neighbourhood of 1000° C. (e.g. 950°—1150° C.) a substance or mixture containing as essential elements one or more alkaline earth metals, one or more halogens, antimony, manganese (if present), phosphorus, and oxygen, the said substance or mixture, which is usually a mixture of several chemical compounds in which the phosphorus and oxygen are present as the radical PO_4, being either not a luminescent material or a luminescent material having luminescent properties other than those of the product of the heating.

In Patent Specification No. 580,363 there is described and claimed a luminescent material comprising a halo-phosphate of the type described above wherein the bivalent metals are mainly one or more alkaline earth metals and wherein part at least of the activator is lead or tin or both, and the alkaline earth metals specifically mentioned, and said to be preferred, are calcium and strontium.

It has now been discovered that good results can be obtained when at least half of the bivalent metal M,M^1 is barium, instead of strontium or calcium, and when the halogen is fluorine or chlorine.

According to the present invention, an artificial luminescent material comprises an activated halo-phosphate (as hereinbefore defined) wherein at least half of the bivalent metal atoms are barium atoms, wherein at least half of the halogen atoms are fluorine atoms or chlorine atoms, or a mixture of atoms of fluorine and chlorine, and wherein the activator includes one or more of antimony, tin, lead.

Manganese may be provided as a secondary activator in order to change the colour of the fluorescence but the magnitude of the change produced is in this case substantially smaller than in the case of calcium halo-phosphates.

According to a feature of the present invention, a luminescent material comprising an activated halo-phosphate (as hereinbefore defined) in which at least half of the bivalent metal atoms are barium atoms, is prepared by heating, preferably to a temperature in the neighbourhood of 1000° C., a substance or mixture containing as essential elements barium; chlorine or fluorine or both; one or more of the elements antimony, lead, tin; phosphorus; oxygen; and possibly manganese, the said substance or mixture being either not a luminescent material or a luminescent material with luminescent properties other than those of the product of the heating.

According to a further feature of the invention, an electric discharge lamp comprises a luminescent material according to the invention as aforesaid, the said material being adapted to be excited to luminescence by the discharge in the lamp.

According to yet another feature of the invention, a cathode ray tube comprises a luminescent material according to the invention as aforesaid, the said material being adapted to be excited to luminescence by the cathode rays in the tube.

Certain methods of preparing fluorescent materials according to this invention will be described by way of example. All of the reagents mentioned are preferably of the highest commercial purity, for example when obtainable they should be of the grade sold under the Registered Trade Mark AnalaR.

Barium fluoride may be prepared as follows: 244 grms. barium chloride ($BaCl_2.2H_2O$) (AnalaR) are dissolved in 1 litre of hot distilled water to form solution A. 100 grms. ammonium fluoride (AnalaR) is dissolved in 250 mls. of hot distilled water to form solution B. 10 mls. of solution A are added to solution B and 10 mls. of solution B are added to solution A. The resulting liquids are filtered and the filtrates are mixed. The precipitate is separated by filtration, washed six times with hot distilled water, dried at 160° C. and ground. Strontium fluoride may be prepared in an analogous manner.

Strontium chloride ($SrCl_2.6H_2O$) is prepared by dissolving strontium carbonate in the calculated quantity of dilute hydrochloric acid and crystallising from this liquor.

Barium phosphate may be prepared as follows: 1180 grms. $BaCO_3$ (AnalaR) is mixed into a slurry with 1500 mls. of cold distilled water to form C. 255 mls. of ortho-phosphoric acid (AnalaR) is diluted to 500 mls. with cold distilled water and called solution D. C is added to solution D slowly and with constant stirring. When effervescence has ceased the liquid is filtered, the precipitate is dried at 160° C. and ground. Strontium phosphate may be prepared from strontium carbonate in an analogous manner.

Antimony tri-oxide may be prepared as follows: 500 grms. antimony trichloride (AnalaR) is dissolved in the minimum amount of cold concentrated hydrochloric acid. Ammonia solution (AnalaR) (S.G. 0.880) is then slowly added with constant stirring until no further precipitation occurs. The precipitate is filtered off and washed six times in boiling distilled water, dried at 160° C. and ground. The resulting white powder may contain a little oxychloride of antimony.

Manganese phosphate may be prepared as follows: 396 gm. di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) (AnalaR) is dissolved in two litres of boiling distilled water to form solution E. 594 gm. manganese chloride (AnalaR) is dissolved in 3 litres of distilled water to form solution F. 10 ml. of solution E is added to solution F, and 10 mls. of solution F to solution E; the resulting liquids are filtered and the filtrates mixed. The precipitate is separated by filtration, washed with boiling distilled water, and dried at 160° C. The dried product is ground.

EXAMPLE I.

If the material required is $3Ba_3(PO_4)_2.1\ BaF_2 + 3\%\ Sb + 1.7\%\ Mn$, the substance to be heated may consist of a mixture of 66.3 grms. barium phosphate, 5.8 grms. barium fluoride, 2.4 grms. antimony tri-oxide and 3.1 grms. manganese phosphate. This mixture is furnaced in a silica boat closed by a glass wool plug at 1000° C. for ½ hour and allowed to cool. When cool the substance is ground and re-furnaced for a further ½ hour at the same temperature.

If necessary a small amount of barium carbonate (AnalaR) or di-ammonium hydrogen phosphate (AnalaR) may be

added to the initial mixture to produce the optimum luminescent efficiency. The reason why such additions may be necessary is that the proportions of BaO and P_2O_5 in the finished product are critical for the best results. It is frequently found that to achieve the optimum result it is necessary to adjust the relative proportions of these two constituents by the addition of one of them to the mixture before furnacing, preferably in the form of barium carbonate or di-ammonium hydrogen phosphate. The quantities of the latter substances to be added have been found to vary between, by weight of the mixture, about 0 and 2% barium carbonate and between 0 and 8% di-ammonium hydrogen phosphate; thus in some cases a small quantity of barium carbonate may be needed and in others a small quantity of di-ammonium hydrogen phosphate will be found to give the best results; the optimum proportions are best determined by preparing a series of sample mixtures containing different additions of barium carbonate or di-ammonium hydrogen phosphate and selecting that composition giving the best result after the two furnacings.

The powder, after the second heat treatment, may be ground, washed and sieved to the required particle size. The powder shows a yellow fluorescence under U.V. light of 2537 Å.

Materials with different luminescent properties may be prepared by partially or completely replacing the barium fluoride by barium chloride and also by increasing or decreasing the percentage of manganese in the initial mixture. The luminescent colours and approximate brightness of some modified compositions are given in the following table:—

Composition	Percentage of Manganese 0	2	5	7.5
3 $Ba_3(PO_4)_2$.1 BaF_2 + 3% Sb	Bright yellow	Moderate yellow (more saturated)	Weak yellow	Weak yellow
6 $Ba_3(PO_4)_2$.1 BaF_2.1 $BaCl_2$ + 3% Sb	Moderate yellow (more saturated)	Weak yellow	Very weak yellow	——
3 $Ba_3(PO_4)_2$.1 $BaCl_2$ + 3% Sb	Weak yellow	Very weak yellow	——	——

EXAMPLE II.

If the material required is $3Ba_3(PO_4)_2$.1 BaF_2 + 5% Pb + 1.7%Mn, the substance to be heated may be a mixture of 66.3 grms. barium phosphate, 5.8 grms. barium fluoride, 3.3 grms. ammonium fluoride (AnalaR), 3.1 grms. manganese phosphate and 5.3 grms. lead nitrate (AnalaR). This mixture is furnaced in a silica boat closed by a glass wool plug at 950° C. for ½ hour. The product may then be ground, washed and sieved to the required particle size. As in the preceding example a small amount of barium carbonate or di-ammonium hydrogen phosphate (usually from 0—2% barium carbonate and 8—0% di-ammonium hydrogen phosphate may be added if necessary to the initial mixture to produce the optimum luminescent efficiency. This powder shows a pinky-red fluorescence under U.V. light of 2537 Å.

EXAMPLE III.

The initial mixture of Example II is modified to give 5% Sn instead of 5% Pb by the addition 6.3 grms. stannous chloride (AnalaR) in place of the lead nitrate, and the method of preparation is otherwise the same as in Example II. This powder shows a yellow-green fluorescence under U.V. light of 2537 Å.

EXAMPLE IV.

If the material required is $6Ba_3(PO_4)_2$.1 BaF_2.1 $BaCl_2$.6 $Sr_3(PO_4)_2$.1 SrF_2.1 $SrCl_2$ +3% Sb+1%Mn, the following mixture is prepared: 33.1 grms. barium phosphate, 25.8 grms. strontium phosphate, 1.5 grms. barium fluoride, 2.0 grms. barium chloride ($BaCl_2.2H_2O$) (AnalaR), 1.0 grms. strontium fluoride, 2.2 grms. strontium chloride ($SrCl_2.6H_2O$), 2.1 grms. antimony trioxide and 2.1 grms. manganese chloride ($MnCl_2.4H_2O$) (AnalaR). This mixture is ground and furnaced in

a silica tube closed by a glass wool plug for half an hour at 1100° C. When cool the mixture is ground and re-furnaced. When again cool the mixture may be ground and washed with distilled water and dried. When excited by short wave U.V. light of 2537 Å this powder shows a yellowy-white luminescence.

If necessary in order to produce the best luminescence a small amount of barium carbonate or di-ammonium hydrogen phosphate may be added before furnacing as in the previous examples.

EXAMPLE V.

If the material required is $6Ba_3(PO_4)_2.1 BaF_2.1 BaCl_2.6 Ca_3(PO_4)_2.1 CaF_2.1 CaCl_2 + 3\%$ Sb + 1% Mn, the following mixture is prepared: 33.1 grms. barium phosphate, 18.6 grms. calcium phosphate, 1.5 grms. barium fluoride, 2.0 grms, barium chloride ($BaCl_2.2H_2O$) (AnalaR), 0.7 grms. calcium fluoride, 1.3 grms. calcium chloride, 1.8 grms, antimony trioxide and 1.8 grms. manganese chloride (AnalaR). The calcium phosphate and fluoride may be prepared as described in Patent Specification No. 578,192. The calcium chloride is dried, of AnalaR grade, and contains about 27.5% water.

This mixture is ground and furnaced in a silica tube closed by a glass wool plug for half an hour at 1100° C. When cool the mixture is ground and re-furnaced. When again cool it may be ground and washed with distilled water and subsequently dried: The powder shows a pale pink luminescence under short wave U.V. radiation of 2537 Å. The content of BaO and P_2O_5 in the finished product may, if necessary, be adjusted as already described.

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. An artificial luminescent material comprising an activated halo-phosphate (as hereinbefore defined) wherein at least half of the bivalent metal atoms are barium atoms, wherein at least half of the halogen atoms are fluorine atoms or chlorine atoms, or a mixture of atoms of fluorine and chlorine, and wherein the activator includes one or more of antimony, tin, lead.

2. An artificial luminescent material according to claim 1 containing manganese as a secondary activator.

3. A method of manufacturing a luminescent material comprising an activated halo-phosphate (as hereinbefore defined) in which at least half of the bivalent metal atoms are barium atoms, comprising heating, preferably to a temperature in the neighbourhood of 1000° C., a substance or mixture containing as essential elements barium; chlorine or fluorine or both; one or more of antimony, lead, tin; phophorus; oxygen; and possibly manganese. the said substance or mixture being either not a luminescent material or a luminescent material with luminescent properties other than those of the product of the heating.

4. A method of manufacturing a luminescent material comprising an activated halo-phosphate (as hereinbefore defined), in which at least half of the bivalent metal atoms are barium atoms, which is carried out substantially as hereinbefore described in Example I, II, III, IV or V.

5. An artificial luminescent material when prepared by the method claimed in Claim 3 or 4.

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

7. A cathode ray tube comprising a luminescent material according to Claim 1, 2 or 5, the said material being adapted to be excited to luminescence by the cathode rays in the tube.

Dated the 28th day of January, 1946.
For the Applicants:
A. F. CORNOCK,
Chartered Patent Agent.

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a silica tube closed by a glass wool plug for half an hour at 1100° C. When cool the mixture is ground and re-furnaced. When again cool the mixture may be ground and washed with distilled water and dried. When excited by short wave U.V. light of 2537 Å this powder shows a yellowy-white luminescence.

If necessary in order to produce the best luminescence a small amount of barium carbonate or di-ammonium hydrogen phosphate may be added before furnacing as in the previous examples.

EXAMPLE V.

If the material required is $6Ba_3(PO_4)_2.1 BaF_2.1 BaCl_2.6 Ca_3(PO_4)_2.1 CaF_2.1 CaCl_2 + 3\%$ Sb + 1% Mn, the following mixture is prepared: 33.1 grms. barium phosphate, 18.6 grms. calcium phosphate, 1.5 grms. barium fluoride, 2.0 grms. barium chloride ($BaCl_2.2H_2O$) (AnalaR), 0.7 grms. calcium fluoride, 1.3 grms. calcium chloride, 1.8 grms, antimony trioxide and 1.8 grms. manganese chloride (AnalaR). The calcium phosphate and fluoride may be prepared as described in Patent Specification No. 578,192. The calcium chloride is dried, of AnalaR grade, and contains about 27.5% water.

This mixture is ground and furnaced in a silica tube closed by a glass wool plug for half an hour at 1100° C. When cool the mixture is ground and re-furnaced. When again cool it may be ground and washed with distilled water and subsequently dried: The powder shows a pale pink luminescence under short wave U.V. radiation of 2537 Å. The content of BaO and P_2O_5 in the finished product may, if necessary, be adjusted as already described.

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. An artificial luminescent material comprising an activated halo-phosphate (as hereinbefore defined) wherein at least half of the bivalent metal atoms are barium atoms, wherein at least half of the halogen atoms are fluorine atoms or chlorine atoms, or a mixture of atoms of fluorine and chlorine, and wherein the activator includes one or more of antimony, tin, lead.

2. An artificial luminescent material according to claim 1 containing manganese as a secondary activator.

3. A method of manufacturing a luminescent material comprising an activated halo-phosphate (as hereinbefore defined) in which at least half of the bivalent metal atoms are barium atoms, comprising heating, preferably to a temperature in the neighbourhood of 1000° C., a substance or mixture containing as essential elements barium; chlorine or fluorine or both; one or more of antimony, lead, tin; phophorus; oxygen; and possibly manganese. the said substance or mixture being either not a luminescent material or a luminescent material with luminescent properties other than those of the product of the heating.

4. A method of manufacturing a luminescent material comprising an activated halo-phosphate (as hereinbefore defined), in which at least half of the bivalent metal atoms are barium atoms, which is carried out substantially as hereinbefore described in Example I, II, III, IV or V.

5. An artificial luminescent material when prepared by the method claimed in Claim 3 or 4.

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

7. A cathode ray tube comprising a luminescent material according to Claim 1, 2 or 5, the said material being adapted to be excited to luminescence by the cathode rays in the tube.

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