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PATENT SPECIFICATION

578,195

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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 luminescent materials that are improvements in or modifications of those described in patent application No. 8308/42 (Serial No. 578,192). The essential feature of those materials is that they comprise an activated halophosphate matrix, in which the metals are alkaline earth metals. It is said that one suitable activator is antimony. The invention relates also to fluorescent lamps and cathode ray tubes containing luminescent materials.

We have now discovered that other useful materials can be obtained by substituting bismuth, partly or wholly, for antimony as the activator of the matrix.

According to the invention a luminescent material comprises a halophosphate matrix containing alkaline earth metals, activated at least in part by bismuth.

When bismuth replaces antimony, the amount of bismuth should be somewhat greater than the amount of antimony replaced. Thus, while 2 to 6% of antimony is preferred, the preferred amount of bismuth, if no antimony is present, may be as high as 7½%.

In Application No. 11918/42 (Serial No. 578,192) it is stated that the introduction of manganese into antimony-activated halophosphates is beneficial. It is also beneficial in the bismuth-activated halophosphates, but its effect is rather different. The introduction of manganese often produces little or no change of the colour of the luminescent light, but it may increase the efficiency of luminescence appreciably.

The use of two or more alkaline earth metals, or two or more halogens, in the same antimony-activated halophosphate is described in Application No. 17405/42 (Serial No. 578,192). The general statements made there are applicable also to bismuth-activated halophosphates.

The materials according to the invention that have been studied chiefly so far are $3\,Ca_3(PO_4)_2$. $1\,CaF_2 + 7\frac{1}{2}\%$ Bi, which gives nearly white luminescent light; $3\,Ca_3(PO_4)_2 + 3\%$ Bi $+ 1\%$ Mn, also giving nearly white light; $3\,Ca_3(PO_4)_2$. $1\,CaCl_2 + 7\frac{1}{2}\%$ Bi $+ 3\%$ Mn, which gives reddish light; and $3\,Ca_3(PO_4)_2$. $1\,CaF_2 + 7\frac{1}{2}\%$ Bi $+ 3\%$ Sb, which gives pale pink light. The excitation in all these cases is by 2537Å radiation. The best methods of preparation appear to be closely analogous to those described in the said Application No. 17405/42 (Serial No. 578,192).

Dated the 3rd day of May, 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 luminescent materials that are improvements in or modifications of those described and claimed in Patent Specification No. 578,192 (Application Nos. 8308/42, 11918/42 and 17405/42). The characteristic feature of those materials, roughly described, is that they are halophosphates, containing

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alkaline earth metals, and that part at least of the activator is antimony. The invention relates also to fluorescent lamps and cathode ray tubes containing luminescent materials.

We have now discovered that other useful materials can be obtained by substituting bismuth, partly or wholly, for antimony as the activator of those halophosphates.

According to the invention a luminescent material according to Claim 1 of the above mentioned Patent Specification No. 578,192 (Application Nos. 8308/42, 11918/42 and 17405/42) is modified by replacing part or all of the antimony by bismuth.

The amount of bismuth should be somewhat greater than the amount of antimony replaced. Thus, while 2 to 6% of antimony is preferred, the preferred amount of bismuth, if no antimony is present, is preferably between $2\frac{1}{2}$ to $7\frac{1}{2}$%.

In the above mentioned Patent Specification No. 578,192 (Application Nos. 8308/42, 11918/42 and 17405/42) it is stated that the introduction of manganese into antimony-activated halophosphates is beneficial. It is often also beneficial in the bismuth-activated halophosphates, either because it changes the colour of the luminescent light, or because it increases the efficiency of luminescence appreciably, or for both reasons, the content of manganese may be between 0 and 10% by weight.

The statements made in the parent specification as to what alkaline earth metals and what halogens are preferable, are true also of the bismuth-activated halophosphates. But the use of any considerable proportion of barium seems to be even less advantageous than in the antimony-activated materials. The methods of preparation described in the said Patent Specification No. 578,192 (Application Nos. 8308/42, 11918/42 and 17405/42) may be used for preparing bismuth-activated halophosphates modified only in that a bismuth compound is substituted for part at least of the antimony compound. Bismuth trioxide is a suitable bismuth compound.

As examples of material according to the invention the following may be given: — 3 $Ca_3(PO_4)_2$. 1 CaF_2 + $7\frac{1}{2}$% Bi, which gives nearly white luminescent light; 3 $Ca_3(PO_4)_2$. 1 CaF_2 + 3% Bi + 1% Mn, giving yellowish light; 3 $Ca_3(PO_4)$. 1 $CaCl_2$ + $7\frac{1}{2}$% Bi + 3% Mn, which gives reddish light; and 3 $Ca_3(PO_4)_2$. 1 CaF_2 + $7\frac{1}{2}$% Bi + 3% Sb which gives nearly white light. The excitation in all these cases is by 2537Å radiation.

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 a halophosphate (as defined in Patent Specification No. 578,192 (application Nos. 8308/42, 11918/42 and 17405/42)), 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 halophosphate is activated by an activator of which part at least is bismuth.

2. A luminescent material according to Claim 1 comprising also manganese.

3. The method of preparing a luminescent material according to Claim 1 which comprises heating a mixture comprising a phosphate of M (as defined in Patent Specification No. 578,192 (application Nos. 8308/42, 11918/42 and 17405/42)), a halide M^1L_2, and bismuth or a compound of bismuth.

4. A method according to Claim 3 wherein the said mixture comprises also manganese or a compound of manganese.

5. The method according to Claim 3 or 4 wherein the said phosphate of M is calcium or strontium phosphate prepared substantially as described in the said Specification.

6. The metod according to Claim 3, 4, or 5 wherein the said component M^1L_2 is calcium or strontium fluoride prepared substantially as described in Patent Specification No. 578,192 (application Nos. 8308/42, 11918/42 and 17405/42).

7. The method according to Claim 4 or 5 wherein the said compound of manganese is a phosphate prepared substantially as described in Patent Specification No. 578,192 (application Nos. 8308/42, 11918/42 and 17405/42).

8. A luminescent material prepared according to Claim 3, 4, 5, 6, or 7.

9. A luminescent material according to Claim 1, 2, or 8, wherein the said M and M^1 are each calcium or strontium or a mixture of calcium and strontium wherein the said L is fluorine or chlorine or a mixture of fluorine and chlorine or a mixture of bromine with either or both of fluorine and chlorine, wherein the content of bismuth is between $2\frac{1}{2}$ and $7\frac{1}{2}$% by weight and wherein the content of manganese is between 0 and 10% by weight.

10. A luminescent material according to Claim 9 whose composition is substantially one of those hereinbefore given by

alkaline earth metals, and that part at least of the activator is antimony. The invention relates also to fluorescent lamps and cathode ray tubes containing luminescent materials.

We have now discovered that other useful materials can be obtained by substituting bismuth, partly or wholly, for antimony as the activator of those halophosphates.

According to the invention a luminescent material according to Claim 1 of the above mentioned Patent Specification No. 578,192 (Application Nos. 8308/42, 11918/42 and 17405/42) is modified by replacing part or all of the antimony by bismuth.

The amount of bismuth should be somewhat greater than the amount of antimony replaced. Thus, while 2 to 6% of antimony is preferred, the preferred amount of bismuth, if no antimony is present, is preferably between 2½ to 7½%.

In the above mentioned Patent Specification No. 578,192 (Application Nos. 8308/42, 11918/42 and 17405/42) it is stated that the introduction of manganese into antimony-activated halophosphates is beneficial. It is often also beneficial in the bismuth-activated halophosphates, either because it changes the colour of the luminescent light, or because it increases the efficiency of luminescence appreciably; or for both reasons, the content of manganese may be between 0 and 10% by weight.

The statements made in the parent specification as to what alkaline earth metals and what halogens are preferable, are true also of the bismuth-activated halophosphates. But the use of any considerable proportion of barium seems to be even less advantageous than in the antimony-activated materials. The methods of preparation described in the said Patent Specification No. 578,192 (Application Nos. 8308/42, 11918/42 and 17405/42) may be used for preparing bismuth-activated halophosphates modified only in that a bismuth compound is substituted for part at least of the antimony compound. Bismuth trioxide is a suitable bismuth compound.

As examples of material according to the invention the following may be given: — 3 $Ca_3(PO_4)_2$. 1 CaF_2 + 7½% Bi, which gives nearly white luminescent light; 3 $Ca_3(PO_4)_2$. 1 CaF_2 + 3% Bi + 1% Mn, giving yellowish light; 3 $Ca_3(PO_4)$. 1 $CaCl_2$ + 7½% Bi + 3% Mn, which gives reddish light; and 3 $Ca_3(PO_4)_2$. 1 CaF_2 + 7½% Bi + 3% Sb which gives nearly white light. The excitation in all these cases is by 2537Å radiation.

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 a halophosphate (as defined in Patent Specification No. 578,192 (application Nos. 8308/42, 11918/42 and 17405/42)), 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 halophosphate is activated by an activator of which part at least is bismuth.

2. A luminescent material according to Claim 1 comprising also manganese.

3. The method of preparing a luminescent material according to Claim 1 which comprises heating a mixture comprising a phosphate of M (as defined in Patent Specification No. 578,192 (application Nos. 8308/42, 11918/42 and 17405/42)), a halide M^1L_2, and bismuth or a compound of bismuth.

4. A method according to Claim 3 wherein the said mixture comprises also manganese or a compound of manganese.

5. The method according to Claim 3 or 4 wherein the said phosphate of M is calcium or strontium phosphate prepared substantially as described in the said Specification.

6. The metod according to Claim 3, 4, or 5 wherein the said component M^1L_2 is calcium or strontium fluoride prepared substantially as described in Patent Specification No. 578,192 (application Nos. 8308/42, 11918/42 and 17405/42).

7. The method according to Claim 4 or 5 wherein the said compound of manganese is a phosphate prepared substantially as described in Patent Specification No. 578,192 (application Nos. 8308/42, 11918/42 and 17405/42).

8. A luminescent material prepared according to Claim 3, 4, 5, 6, or 7.

9. A luminescent material according to Claim 1, 2, or 8, wherein the said M and M^1 are each calcium or strontium or a mixture of calcium and strontium wherein the said L is fluorine or chlorine or a mixture of fluorine and chlorine or a mixture of bromine with either or both of fluorine and chlorine, wherein the content of bismuth is between 2½ and 7½% by weight and wherein the content of manganese is between 0 and 10% by weight.

10. A luminescent material according to Claim 9 whose composition is substantially one of those hereinbefore given by

way of example.

11. An electrical discharge lamp comprising a luminescent material according to Claim 1, 2, 8, 9, or 10 adapted to be excited by the discharge in the lamp.

12. A cathode ray tube comprising luminescent material according to Claim 1, 2, 8, 9, or 10 adapted to be excited by the cathode rays in the tube.

Dated the 8th day of March, 1944.
For the Applicants,
A. F. CORNOCK,
Chartered Patent Agent.

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