Government of India, The Patent Office, 214, Acharya Jagadish Bose Road, Calcutta-17. Complete specification No.141491 dated 3rd May 1975. Application Mxx and Provisional specification No.324/Cal/1974 dated 15th February 1974. Acceptance of the complete specification advertised on 12th March 1977.

Index at acceptance - 39E [III]
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IMPROVEMENTS IN OR RELATING TO CALCIUM HALOPHOSPHATE PHOSPHOR FOR USE IN FLUORESCENT TUBELIGHTS.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification describe the nature of this invention.

This is an invention by CHITTARI VENKATA SURYANARAYANA, Scientist, MOHAMMED IFTIKHAR AHMED SIDDIQI, Scientist, NAGAMONY RAJARAM, Scientist, RAMAYYAR LAKSHMINARAYANAN, Senior Scientific Assistant and VEDARAMAN SUNDARAM, Senior Laboratory Assistant, all of Central Electrochemical Research Institute, Karaikudi-3, xxxxx Tamil Nadu, India, all Indian citizens.

PRICE Rs.-.00

This invention relates to improvements in or relating to the preparation of calcium halophosphate phosphors $3\ Ca_3(PO_4)_2$, $Ca(Cl,F)_2$:Sb, Mn mainly for use in fluorescent tubelights. More particularly, the invention relates to a method of making calcium halophosphate phosphor that emits in the yellow regin of the visible spectrum; the luminescent phosphor of this invention has such characteristics that its usefulness is indicated in the fluorescent tubelights when used either singly to give a yellow colour, or as an admixture to a light blue calcium halphosphate phosphor in suitable ratios, the blend then giving a daylight colour of a most acceptable spectral energy distribution.

In order to obtain a spectral energy distribution not obtainable by using a single halophosphate composition in the fluorescent tubelights, methods are reported wherein a green-emitting phosphor such as zinc orthosilicate, ablue-

emitting phosphor such as $CaWO_4$, and a red-emitting phosphor, either one or more, are used additionally. However, this has the drawback that a different class of phosphor may give rise to an inhomogenous blend due to differences such as density, particle size etc., and as it may also cause segregation in slurry-making, it may give rise to 'spottiness'.

The work, which is the subject matter of the patent, is subsequent to an earlier specification No.133367 dated 27.10.1971 on luminescent materials (phosphors) for use in fluorescent tubelights; the said earlier specification was concerned with the preparation of a range of calcium halophosphate phosphors, which on excitation by 2537 Å of Hg (the predominant radiation in a low pressure Hg vapouf discharge tube), give 'light blue', 'daylight', or 'warm-white' emission.

Whereas making of fluorescent tubelights emitting in the yellow region of the visible spectrum is known, wherein generally a daylight phosphor composition is used in combination with a suitable dye, so as to give a filtered yellow emission, this is open to the objection that the intensity gets considerably reduced.

The object of this invention is to work out a method of making a calcium halophosphate phosphor that emits in the yellow region of the visible spectrum with a good intensity.

In this background, the present invention provides with a straighforward method of making a calcium halophosphate phosphor, activated by Sb and Mn that emits in the yellow region of the visible spectrum. The phosphor resulting from the present invention, having a composition corresponding to $3\ Ca_3(PO_4)_2,(Ca/F)_2$: Sb, Mn, on excitation by 2537 Å of Hg, gives emission of yellow colour in the range of 5000-6000 Å, with a peak emission at 5600 Å. The product has the necessary characteristics of a good phosphor, such as fine particle size, white body colour, stability in Hg

vapour and other conditions of discharge in a fluorescent tube (Example I).

To these ends, the invention broadly consists in taking a mixture of high purity luminescent grade raw materials, for instance, calcium hydrogen phosphate, calcium carbonate, calcium fluride, antimony oxide and manganese phosphate, so as to give a matrix of the general formula 3 $Ca_3(PO_4)_2$, $Ca(ClF)_2$: Sb, Mn wherein the M/P ratio is in the vicinity of 4.9/3, antimony is about 1% and Mn is in the range 1.0 to 2.5% making a well mixed slurry of the same with the addition of suitable quantity of distilled water, drying it and heating the mix, in order to obtain a solid state reaction, in a closed silica crucible in a furnace in the range of 900-1250°C preferably close to about 1100°C, for a period of time depending on the quantity of the materials and subsequently air-quenching the same.

We have found that the product of our invention is ideally suited for making a blend wherein it is admixed with a light blue-emitting calcium halphosphate phosphor (for instance, the light blue reported in our specification 133367) in a suitable ratio such a phosphor blend gives a spectral energy distribution comparable with a commercial phosphor sample of a most widely accepted colour rendering. The usefulness of this blend is thus indicated as a coating in the fluorescent tubelights (Example II).

Having described the method of our present invention, we give the following example to illustrate the same:

Example I

Calcium halophosphate phosphor emitting in the Yellow range of visible spectrum:

The following composition is used :

$CaHPO_4$	2.4550 gm
$CaCO_3$	0.6380 gm

CaF_2	0.2167 gm
Sb_2O_3	0.0077 gm
$Mn_3(PO_4)_2$	0.1295 gm

With the addition of about 10 cc of distilled water the composition is mixed into a slurry. It is finely ground in an agate mortar. The mix is heated in a closed silica vessel in a range of temperature between 900-1250°C, preferably in the vicinity of about 1100°C, for about 15 minutes, air quenched and finely ground after cooling. A typical spectral energy distribution of this composition is given in figure 1.

Example II

Calcium halophopsphate phosphor 'daylight' (Blend)

Constituent (i) : Calcium halophosphate phosphor emitting in the yellow range (as made in Example I)

Constituent (ii): Calcium halophosphate phosphor 'light blue' (as in specification No.133367). For instance, the following composition:

$CaHPO_4 2H_2O$	1.2908 gm
$CaCo_3$	0.3428 gm
CaF_2	0.0893 gm
$SrCl_2\ 6H_2O$	0.07992 gm
Sb_2O_3	0.01749 gm

(The composition is processed in the manner of Example I)

Equal weights of constituent (i) and (ii) are then taken.

The blend is thoroughly mixed and ground. Typical spectral energy distribution curves of the constitutents (i) and (ii) are given in Figures 1 and 2 respectively. The spectral energy distribution of a typical resultant blend is given in figure 3.

The following are among the advantages of the invention:

1 The present invention of making calcium halophosphate phosphor for use in fluorescent tubelights results in the production of a phosphor of good quality, giving a high intensity of emmission in the yellow region of the visible spectrum, on excitation by 2537 $\overset{o}{A}$ of Hg.

2. The invention makes possible the production of such a phosphor without the use of an external atmosphere such as nitrogen used conventionally.

3. The invention provides with a method of making a calcium halophosphate yellow-emitting phosphor, which, in admixture in a suitable ratio to a 'light-blue' phosphor of the calcium halophosphate group, results in a blend, giving, on excitation by 2537 $\overset{o}{A}$, the desired spectral energy distribution corresponding to a 'daylight' of the most acceptable type in general use in the fluorescent tubelights.

Reference

Indian Patent No.133367 dated 27.10.1971

Dated this 11th day of February, 1974.

Sd/-
Asstt.Patents Officer,
Council of Scientific & Industrial Research

THE PATENTS ACT 1970

COMPLETE SPECIFICATION

(See Section 10)

IMPROVEMENTS IN OR RELATING TO CALCIUM HALOPHOSPHATE PHOSPHOR FOR USE IN FLUORESCENT TUBELIGHTS

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, an Indian registered body incorporated under the Registration of Societies Act (ACT XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :-

This is an invention by CHITTARI VENKATA SURYANARAYANA, Scientist, MOHAMMED IFTIKHAR AHMED SIDDIQUI, Scientist, NAGAMONY RAJARAM, Scientist, RAMAYYAR LAKSHMINARAYANAN, Senior Scientific Assistant and VEDARAMAN SUNDARAM, Senior Laboratory Assistant, all of Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, India, all Indian citizens.

This invention relates to improvements in or relating to the preparation of calcium halophosphate phosphors 3 $Ca_3(PO_4)_2$, $Ca(Cl,F)_2$:Sb, Mn mainly for use in fluorescent tubelights. More particularly, the invention relates to a method of making calcium halophosphate phosphor that emits in the yellow region of the visible spectrum; the luminescent phosphor of this invention has such characteristics that its usefulness is indicated in the fluorescent tubelights when used either singly to give a yellow colour, or as an admixture to a light blue calcium halophosphate phosphor in suitable ratios, the blend then giving a daylight colour of a most acceptable spectral energy distribution.

Whereas making of fluorescent tubelights emitting in the yellow region of the visible spectrum is known, wherein generally a daylight phosphor composition is used in combination with a

suitable dye, so as to give a filtered yellow emission, this is open to the objection that the intensity gets considerably reduced. In earlier processes, invariably, nitrogen gas was passed during heating.

The object of this invention is to work out a method of making a calcium halophosphate phosphor that emits in the yellow region of the visible spectrum with a good intensity.

To these ends, the invention broadly consists in taking a mixture of high purity luminescent grade raw materials, for instance, calcium hydrogen phosphate, calcium carbonate, calcium fluoride, antimony oxide and manganese phosphate, so as to give a matrix of the general formula 3 $Ca_3(PO_4)_2$, Ca (Sl, F)$_2$: Sb, Mn wherein the metal: phosphorous ratio is in the vicinity of 4.9/3, antimony is about 1% and Mn is in the range 1.0 to 2.5%, making a well mixed slurry of the same with the addition of suitable quantity of distilled water, drying it and heating the mix, in order to obtain a solid state reaction, in a closed silica crucible in a furnace in the range of 900-1250°C preferably close to about 1100°C, for a period of time depending on the quantity of the materials and subsequently air-quenching the same. The resulting material under excitation gives luminescence in the yellow region of the spectrum.

We have found that the product of our invention is ideally suited for making a blend wherein it is admixed with a light blue-emitting calcium halophosphate phosphor (for instance, the light blue phosphor of our invention according to India Patent No.133367), in a suitable ratio; such a phosphor blend gives a spectral energy distribution comparable with a commercial phosphor sample of a most widely accepted colour rendering. The usefulness of this blend is thus indicated as a coating in the fluorescent tubelights (Example II

Having described the method of our present invention, we give the following example to illustrate the same:

EXAMPLE I

Calcium halophosphate phosphor emitting in the yellow range of visible spectrum:

The following composition is used:

$CaHPO_4$	2.4550 gm
$CaCO_3$	0.6380 gm
CaF_2	0.2147 gm
Sb_2O_3	0.0277 gm
$Mn_3(PO_4)_2$	0.1295 gm

With the addition of about 10 cc of distilled water, the composition is mixed into a slurry. It is finely ground in an agate mortar. The mix is heated in a closed silica vessel in a range of temperature between 900-1250°C, preferably in the vicinity of about 1100°C, for about 15 minutes, air quenched and finely ground after cooling. A typical spectral energy distribution of this composition is given in the accompanying drawings of provisional specification figure 1 wherein the abscisse gives the wave length in mu and the ordinate gives the intensity in arbitrary units.

EXAMPLE II

Calcium halophosphate phosphor 'daylight' (Blend)

Constituent (i) : Calcium halophosphate phosphor emitting in the yellow range (as made in example I).

Constituent (ii) : Calcium halophosphate phosphor 'light blue' (as in specification No.133367). For instance, the following composition:

$CaHPO_4$	1.2908 gm
$CaCO_3$	0.3428 gm
CaF_2	0.0893 gm
$SrCl_2\ 6H_2O$	0.07992 gm
Sb_2O_3	0.01749 gm

(The composition is processed in the manner of Example I)
Equal weights of constituent (i) and (ii) are then taken.

The blend is thoroughly mixed and ground. Typical spectral energy distribution curves of the constituents (i) and (ii) are given in the accompanying drawings of provisional specification figures 1 and 2 respectively. The spectral energy distribution of a typical resultant blend is given in the accompanying drawings of the provisional specification figure 3.

The following are among the advantages of the invention:

1 The present invention of making calcium halophosphate phosphor for use in fluorescent tubelights results in the production of a phosphor of good quality, giving a high intensity of emission in the yellow region of the visible spectrum, on excitation by 2537 Å of Hg.

2 The invention makes possible the production of such a phosphor without the use of an external atmosphere such as nitrogen used conventionally.

3 The invention provides with a method of making a calcium halophosphate yellow-emitting phosphor, which, in admixture in a suitable ratio to a 'light-blue' phosphor of the calcium halophosphate group, results in a blend, giving, on excitation by 2537 Å, the desired spectral energy distribution corresponding to a 'daylight' of the most acceptable type in general use in the fluorescent tubelights.

Having fully described our invention and the method of practising the same

We claim:

1. A process of making calcium halophosphate phosphor emitting in the yellow region of the visible spectrum, having a composition corresponding to $3\,Ca_3(PO_4)_2\,CaF_2$: Sb, Mn, which comprises taking a mixture of high purity luminescent grade raw materials, for instance, calcium hydrogen phosphate, calcium carbonate, calcium fluoride, antimony oxide and manganese phosphate, so as to give a

matrix of the general formula 3 $Ca_3 (PO_4)_2$, Ca (Cl, F)$_2$: Sb, Mn wherein the metal:phosphorous ratio is in the vicinity of 4.9/3, antimony is about 1% and Mn is in the range 1.0 to 2.5% making a well mixed slurry of the same with the addition of suitable quantity of distilled water, drying it and heating the mix, in order to obtain a solid state reaction, in a closed silica crucible in a furnace in the range of 900-1250°C preferably close to about 1100°C, for a period of time depending on the quantity of the materials and subsequently air-quenching the same: the resulting material under excitation gives luminescence in the yellow region of the spectrum.

Dated this 20th day of April, 1975.

Sd/-
PATENTS OFFICER
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

GIPPP/(C.P & D.C.I)/79-80/150

PROVISIONAL SPECIFICATION

COUNCIL OF SCIENTIFIC &
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No. 141491.

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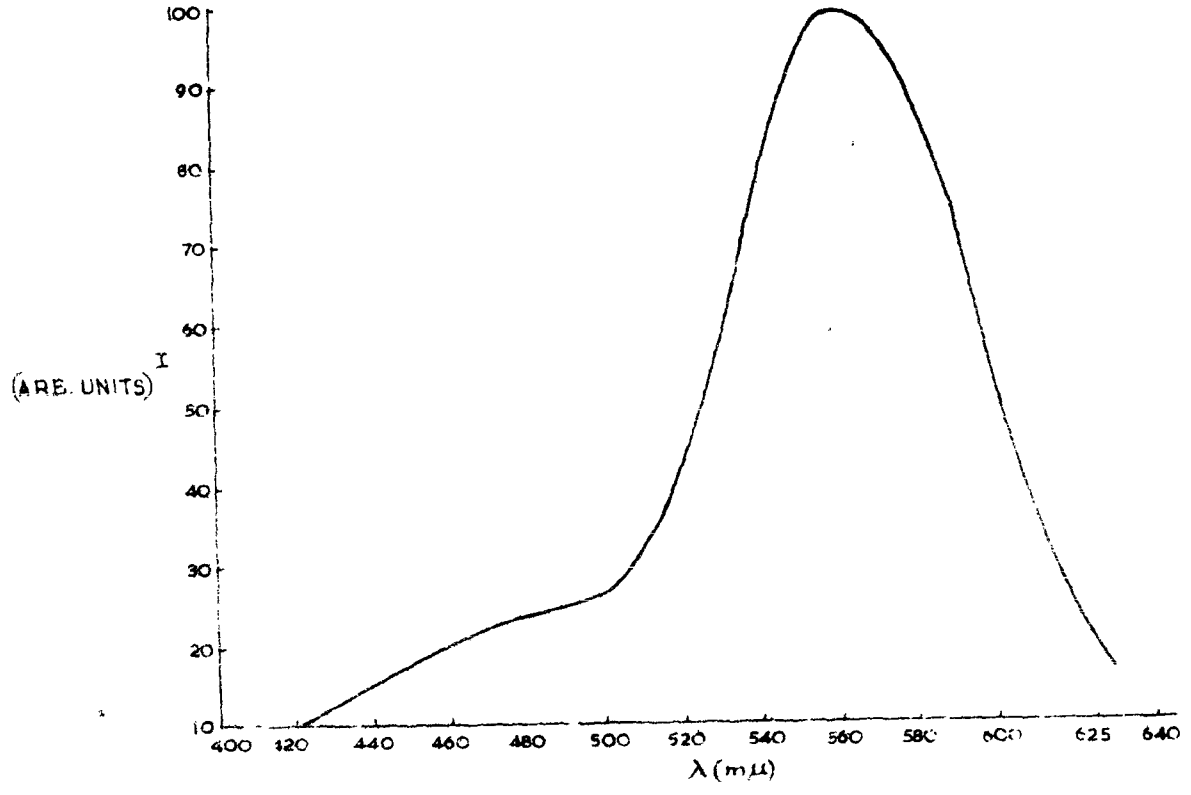

FIG. 1

R S. PAI,
PATENTS OFFICER.
C.S.I.R

PROVISIONAL SPECIFICATION

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

No. 141491.

No OF SHEETS: 3
SHEET No. 2

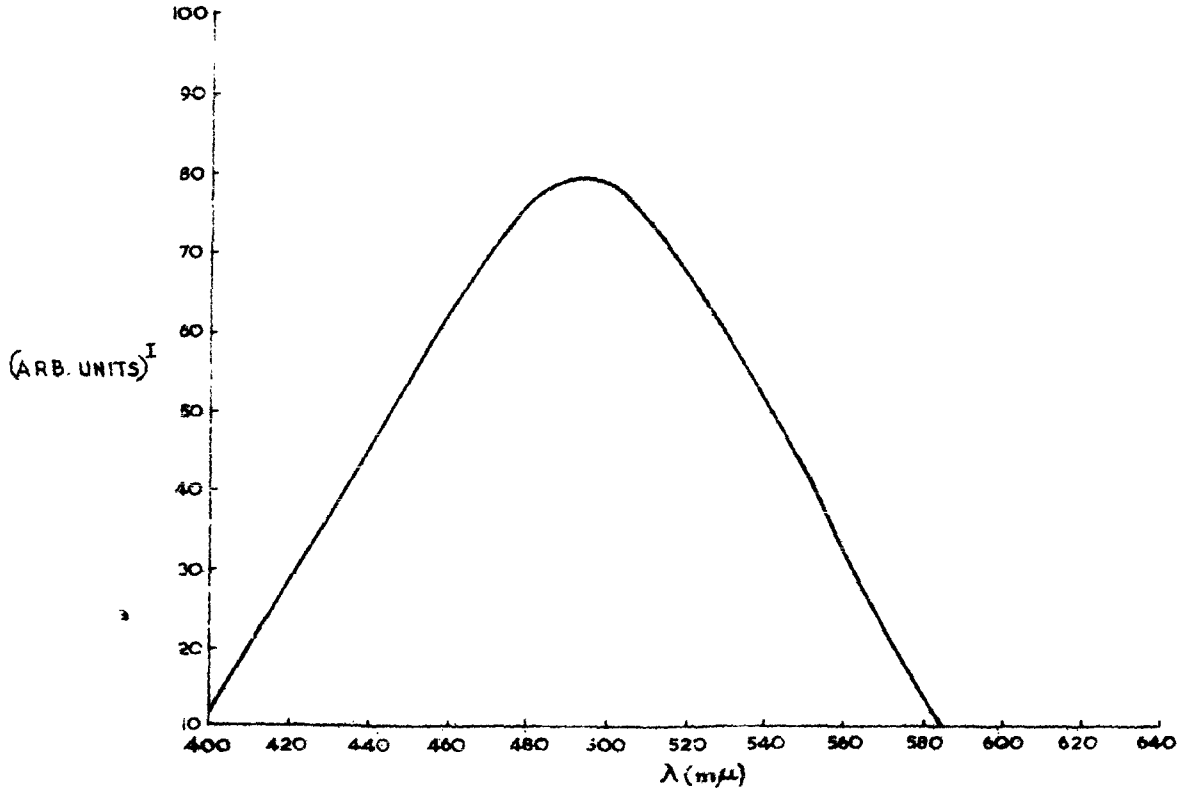

FIG. 2

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PROVISIONAL SPECIFICATION

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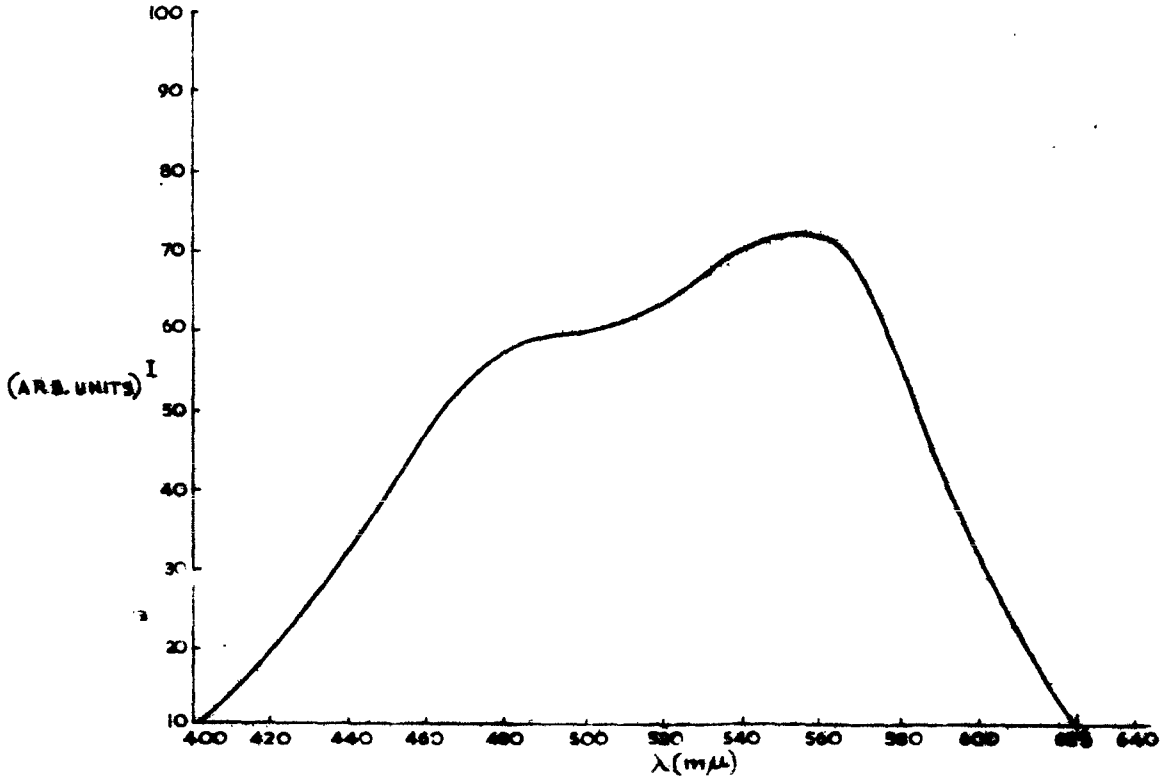

FIG.3

for PATENTS OFFICER,
C.S.I.R.