GOVERNMENT OF INDIA: THE PATENT OFFICE, 214, ACHARYA JAGADISH BOSE ROAD, CALCUTTA-17.

Complete Specification No. 139833, dated 26th September, 1974. Application and Provisional Specification No. 1478/Cal/1973, dated 26th June, 1973. Acceptance of the Complete Specification advertised on 7th August, 1976.

Index at acceptance—121 [LXIII(2)]

International classification—Co9K1/28

PROVISIONAL SPECIFICATION

"IMPROVEMENTS IN OR RELATING TO CALCIUM TUNGSTATE BLUE PHOSPHOR OF DIFFERENT SHADES"

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 describes the nature of this invention :—

Tbis is an invention by CHITTARI VENKATA SURYANARAYANA, Scientist, MOHAMMED IFTIKHAR AHMED SIDDIQI, Scientist, NAGAMONY RAJARAM, Scientist, RAMAYYAR LAKSHMINARAYANAN, Senior Scientific Assistant, Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu and RAMIAH KALYANASUNDARAM, Assistant Professor of Chemistry, Government Arts College, Salem, Tamil Nadu—all Indian citizens.

This invention relates to improvements in or relating to the preparation of luminescent calcium tungstate blue phosphors of different shades mainly for use in fluorescent tubelights, as also in cathodo-luminescence and X-ray fluoroscopy.

Hitherto the luminescent materials, including phosphors for tube-lights were largely imported; moreover, neither the technical nor the patent literature gives complete details on preparation of these materials, which process is a delicate balance of several parameters, such as matrix composition, concentration of one or more activators, the temperature at which the phosphor is heated to bring about the solid state reaction.

The work, which is the subject matter of this patent, is subsequent to an earlier specification No. 113869, dated January 3, 1968 on calcium tungstate blue phosphor (pure); the said earlier specification was concerned with the preparation of a calcium tungstate blue phosphor (pure) which on excitation by 2537 Å of Hg (the predominant radiation in a low pressure Hg vapour discharge tube) has the following luminescence characteristics :

Colour	Deep Blue
Peak	440 μ
Colour co-ordinates :	x = 0·1645, y = 0·1845
Colour purity . .	71·77%

This is open to the objection that different shades in the blue colour are not available.

The object of this invention is to work out optimum conditions in preparing calcium tungstate blue phosphor, variously activated, to give different shades in the blue colour range.

In this background, the present invention provides with a straightforward method of making a calcium tungstate blue phosphor, activated by lead and cadmium. The phosphors resulting from present inbention, having a composition, corresponding to $CaWO_4$: Pb (0.01) and $CaWO_4$: Cd (0.01), Ca and WO_4 in stoichiometric proportions and Pb and Cd in mole per cent given in brackets, on excitation by 2537 Å, give emission of blue colour, of shades different from that of $CaWO_4$ (pure). The concentration of activators may change in the renge 0.01 to 1.0 mole per cent. The product has a fine particle size and a good white body colour; it is stable in Hg vapour and other conditions of discharge in a fluorescent tube. The intensity of emission is comparable with that of either the calcium tungstate (pure) blue phosphor or the imported ones of corresponding shades; in the case of Pb-activated or Cd-activated Ca/WO_4 phosphor of present invention, the activators, while shifting the emission to slightly longer wavelengths, also serve to enhance the absorption of 2537 Å, and thereby increase appreciably the intensity of emission.

To these ends the invention broadly consists in taking a mixture of a calcium oxide containing substance like $CaCO_3$ and a tungstic oxide containing substance like tungstic acid in near stoichiometric proportions (1:1) to which a trace of suitable activator such as Pb and Cd in the range given above would bave deen added, making a slurry drying at 110°C. and subsequently firing the same in the range of temperatures between 800°—1100°C for a time depending upon the quantity of materials.

The following typical examples are given by way of illustrating the invention :

Example I

0·991 gm of purified calcium carbonate ($CaCO_3$), 2·499 g of extra pure (*viz.* E. Merck) tungstic acid (H_2WO_4), and 0·033 g of lead nitrate ($Pb(NO_3)_2$), were mixed and made into a slurry by grinding with a suitable quantity of water and dried at 110°C. in an air oven until the mixture became as nearly white as possible. The thoroughly ground powder was taken in a silica dish and heated at a temperature in the range of 800—1100°C. preferably at about 1000°C for about 15 minutes. The product was suddenly cooled in air. When the product attained room temperature, it was pulverised to pass a 300 mesh seive.

Example II

Batch Composition :

$CaCO_3$	=	0·99 g
H_2WO_4	=	2·499 g
$Cd(NO_3)_2$	=	0·024 g

The phosphor was prepared as in Example I.

The phosphors, thus prepared when excited by ultraviolet radiation of 2537 Å, give fluorescence in the visible region of blue, with the peak emission at 4700Å (Example I) anb 4400 Å (Example II) respectively.

The relative spectral energy distribution of the phosphor powder in the visible was measured under excitation with a monochromatic 2537 Å radiation. The fluorescence emission in the visible was measured with a Beckman Quartz spectrophotometer from 350μ to 600 μ. (The spectral energy distributions of emission of the phosphors of examples I and II, $CaWO_4$: Pb and

$CaWO_4$: Cd respectively are given with reference to the accompanying drawings in the figures 1 and 2).

A comparative study of the chromaticity of these two phosphors with the $CaWO_4$ (pure) prepared earlier, is shown in the following table:—

TABLE

Comparison of Chromaticity Data of Phosphors

Phosphor sample	Peak Wavelength mμ	Colour co-ordinates X	Y	Colour purity %
1. Calcium tungstate pure	440	0·1645	0·1845	71·77
2. $CaWO_4$: Pb (0.01)	470	0.1963	0.2768	52.78
3. $CaWO_4$: Cd (0·01)	440	0·1829	0·2123	62·6

The following are among the main advantages of the invention :—

1. The invention provides with a straightforward method of making calcium tungstate $CaWO_4$ blue phosphors, activated with Pb or Cd, of various shades, of high efficiency, mainly for use in fluorescent tubelights, wherein, on excitation by Hg radiation of 2537 Å, these give emission in the visible range of 3500 Å 6000 Å repectively.

2. The invention is a process of making the calcium tungstate blue phosphors of various shades, $CaWO_4$: Pb and $CaWO_4$: Cd indigenously.

Dated this 16th day of June, 1973.

Sd./-

ASST T. PATENTS OFFICER,
Council of Scientific and Industrial Research.

COMPLETE SPECIFICATION

"IMPROVEMENTS IN OR RELATING TO CALCIUM TUNGSTATE BLUE PHOSPHOR OF DIFFERENT SHADES"

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 SIDDIQI, Scientist, NAGAMONY RAJARAM, Scientist, RAMAYYA LAKSHMINARAYANAN, Senior Scientific Assistant, all of the Central Electrochemical Research Institute, Karaikuri-3, India, and RAMIAH KALYANASUNDARAM, Assistant Professor of Chemistry, Government Arts College, Salem, Tamil Nadu, all Indian citizens.

This invention relates to improvements in or relating to the preparation of luminescent calcium tungstate blue phosphors of different shades mainly for use in fluorescent tubelights, as also in cathodoluminescence and X-ray fluoroscopy.

Luminescent materials, including phosphors for tubelights are largely imported; moreover, neither the technical nor the patent literature gives complete details on preparation of these materials, which process is a delicate balance of several parameters, such as matrix composition, concentration of one or more activators, the temperature at which the phosphor is heated to bring about the solid state reaction.

The work, which is the subject matter of this patent, is subsequent to an earlier specification No. 113869, dated January 3, 1968 on calcium tungstate blue phosphor (pure) the said earlier specification was concerned with the preparation of a calcium tungstate blue phospor (pure) which on excitation by 2537 A of Hg (the predominant radiation in a low pressure Hg vapour discharge tube) has the following luminescence characteristics :

Colour	Deep blue
Peak	440 mμ
Colour co-ordinates	X=0·1645, y=0·1845
Colour purity . .	71·77%

However, it is very often desirable to have different shades in the blue colour range, for use in different climatic environments and consumer requirements.

The object of this invention is to work out optimum conditions in preparing calcium tungstate blue phosphor, variously activated, to give different shades in the blue colour range.

In this background, the present invention provides with a method of making a calcium tungstate blue phosphor, activated by lead and cadmium.

According to the present invention, there is provided a process of making calcium tungstate blue phosphors of varying shades of bluish white, having a composition corresponding to $CaWO_4$: Pb (0.01), or $CaWO_4$: Cd (0.01), which comprises making a slurried mix of substances, namely, calcium carbonate ($CaCO_3$), and tungstic acid (H_2WO_4) in near stoichiometric ratio of 1:1, wherein the activetor, namely either Pb or Cd is in the optimum ratio of 0.01 mole, is added drying and then subjecting the same to heating ina silica crucible to a high temperature in the range of 800—1100°C, but preferably in the vicinity of 1000°C for a period of time depending upon the quantity of the material and pulverising, characterised in that the slurried mass is dried to whiteness at about 110°C, further characterised in that the heated mass obtained after heating at about 1000°C is quenched in air to room temperature prior to pulverising. Such a resulting material is luminescent mainly to 2537 Å radiation, the colour of luminescence emission being in the bluish white region of visible radiation.

The phosphors resulting from our invention, having a composition corresponding to $CaWO_4$: Pb (0·01) and $CaWO_4$: Cd (0·01), Ca and WO_4 in stoichiometric proportions and Pb and Cd in mole percent given in brackets, on excitation by 2537 Å give emission of blue colour, of shades different from that of $CaWO_4$ (pure), the bluish white content of the luminescence emission of either being higher than $CaWO_4$ (pure), which latter gives a deep blue. Also, the bluish white content is greater when Pb is used as the activator, than when Cd is used as such. The product has a fine particle size and a good white body colour; it is stable in Hg vapour and other conditions of discharge in a fluorescent tube. The intensity of emission is comparable with that of either the calcium tungstate (pure) blue phosphor or the imported ones

of corresponding shades; in the case of Pb-activated or Cd-activated $CaWO_4$ phosphor of our invention, the activators, while shifting the emission to slightly longer wave-lengths, also serve to ennance the absorption of 2537 Å, and thereby increase appreciably the intensity of emission.

The process broadly consists in taking a mixture of a calcium oxide-containing substance like $Ca\ CO_3$ and a tungstic oxide-containing substance like $H_2\ WO_4$ in near stoichiometric proportions, to which a trace, of suitable activator such as Pb or Cd would have been added, making a slurry, drying at 110°C and subsequently heating the same in the range of temperatures between 800—1100°C for a time depending upon the quantity of materials.

The following typical examples are given by way of illustrating the invention :

Example 1

0·991 g. of purified calcium carbonate ($Ca\ CO_3$), 2·499 g. of extra pure (viz. E. Merck) tungstic acid ($H_2\ WO_4$), and 0·33 g. lead nitrate $Pb\ (NO_3)_2$, were mixed and made into a slurry by grinding with a suitable quantity of water and dried at 110°C in an air oven until the mixture became as nearly white as possible. The thoroughly ground powder was taken in a silica dish and heated at a temperature in the range of 800—1100°C, preferably at about 1000°C for about 15 minutes. The product was quenched in air. When the product attained room temperature, it was pulverised to pass a 300 mesh sieve.

Example 2

Batch composition :

$Ca\ CO_3$	=	0·990 g.
H_2WO_4	=	2.499 g.
$Cd\ (NO_3)_2$	=	0·024 g.

The phosphor was prepared as in example 1.

The phosphors, thus prepared when excited by ultraviolet radiation of 2537 Å, give fluorescence in the visible region of blue, with the peak emission at 4700 Å. (Example 1) and 440 Å (Example 2) respectively

The relative spectral energy distribution of luminescence emission of the phosphors in the visible, under excitation with a monochromatic 2537 Å radiation, was measured with a Beckman Quartz Spectrophotometer from 350 mμ to 600 mμ. (The spectral energy distribution of emission of the phosphors of examples 1 and 2, $Ca\ WO_4$: Pb and $Ca\ WO_4$: Cd are given in the accompanying drawings of Provisional Specification figures 1 and 2 respectively, wherein the abscissa gives the wavelengths in mμ and the ordinate gives the intensity in arbitrary units).

A comparative study of this chromaticity of these two phosphors with the $Ca\ WO_4$ (pure) prepared earlier, is shown in the following table :

TABLE

Comparison of Chromaticity Data of Phosphors

Phosphor sample	Peak wavelength mμ	Colour co-ordinates X	Y	Color purity%
1. Calcium tungstate (pure)	440	0.1645	0.1845	71.77
2. $CaWO_4$: Pb (0.01)	470	0·1963	0.2768	52.78
3. $CaWO_4Cd$ (0.01)	440	0·1829	0.2123	62.6

While we have experimented with several concentrations of the activators, we have found that the particular concentrations reported in Examples 1 and 2 give about the best intensity. Similarly, while we have tried some variations in the other parameters, the ones reported in the examples are near optimum. We have also found that trace impurity additions of ions such as Sb, Ga, Tl, In, Th, Ti, Ce have the effect of decreasing the intensity of emission (in the order reported) as compared to the $CaWO_4$ (pure) phosphor.

The following are among the main advantages of the invention :

1. The invention provides with a straightforward method of making calcium tungstate $CaWO_4$ blue phosphors activated with Pb or Cd, of various shades, of high efficiency, mainly for use in fluorescent tube-lights, wherein, one excitation by Hg radiation of 2537 Å, these give emission in the visible range of 3500 Å to 6000 Å respectively.

2. The invention is a process of making calcium tungstate blue phosphors of various shades, $CaWO_4$: Pb and $CaWO_4$: Cd indigenously.

Having fully described our invention and the method of practising the same, we claim :—

WE CLAIM :

1. A process of making calcium tungstate blue phosphor of varying shades of bluish white, having a composition corresponding to $CaWO_4$: Pb (0·01) or $CaWO_4$: Cd (0·01), which comprises making a slurried mix of substances namely calcium carbonate ($CaCO_3$), and tungstic acid (H_2WO_4) in near stoichiometric ratio of 1 : 1 wherein the activator namely either Pb or Cd is in the optimum ratio of 0·01 mole in the form of salt is added, dried and then subjecting to heating in a silica crucible to a high temperature in the range of 800 to 1100°C but preferably in the vicinity of 1000°C for a period of time depending upon the quantity of the material, and pulverizing the same characterised in that the slurried mass is dried to whiteness at about 110°C, further characterised in that the heated mass obtained after heating at about 1000°C is quenched in air to room temperature prior to pulverising.

Dated this 12th day of September, 1974.

Sd/-
PATENT OFFICER,
Council of Scientific and Industrial Research

GIPN—S5—[23] 10 CP & D Cal./76—11-1-77—150

COMPLETE SPECIFICATION

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

No. 1478/Cal/73 No. 139833.

Nº OF SHEETS:-2.
SHEET Nº :- 1.

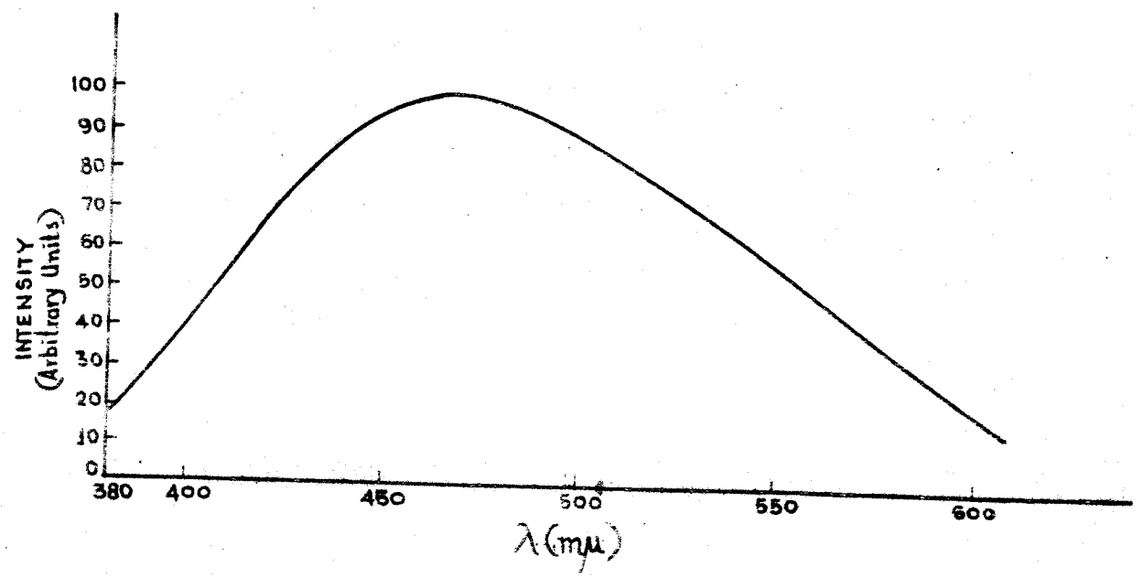

FIG. 1.

R B Pai

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

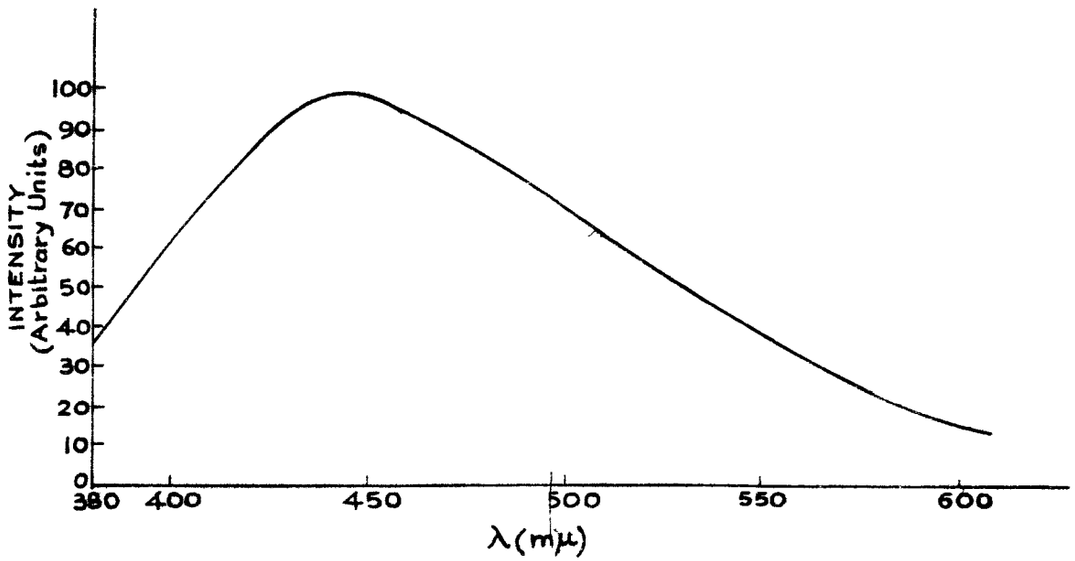

FIG 2

R Bhaskara Pai

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