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## PROVISIONAL SPECIFICATION

### IMPROVEMENTS IN OR RELATING TO THE PREPARATION OF CALCIUM TUNGSTATE BLUE PHOSPHOR

COUNCIL OF SCIENTIFIC & 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:—

This is an invention by CHITTARI VENKATA SURYANARAYANA Scientist, MOHAMMED IFTIKHAR AHMED SIDDIQ  
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This invention relates to improvements in or relating to the preparation of luminescent calcium tungstate blue phosphor.

Luminescent phosphors in general are characterised by methods of preparation which are rather critical if efficient luminescence is to be obtained. The purity of starting materials, the optimisation of compositions and control of parameters like temperature in conducting the associated solid state reactions are all not openly available either in publications or patents. The present invention is a process evolved to get the best luminescent calcium tungstate phosphor particularly useful in fluorescent lamps wherein the exciting radiation is mainly the 2537 Å line of mercury and in general useful in other situations where the exciting source may be electrons or X-rays. The blue calcium tungstate phosphor, for example, being used in fluorescent tubes, is at present imported from abroad. The exact method of processing the phosphor useful in tubelights is not clearly given in published literature either in journals or in patents. For example, an important parameter like the temperature of firing to bring about the solid state reactions has been given as between 300-1100°C. In this background, the object of this invention is to work out optimum conditions in preparing calcium tungstate phosphor capable of giving luminosity comparable with that of the calcium tungstate phosphor being so far imported.

To these ends, the invention broadly consists in taking a mixture of calcium carbonate and tungstic acid or oxide in near stoichiometric proportions, making a slurry and subsequently heating and firing the same in the range of temperature between 800-1100°C for a time depending upon the quantity of materials started with.

The following typical examples are given to illustrate the invention:

#### Example I

100g. of purified calcium carbonate (starting material being B. D. H., A. R. quality) and 250 g. of extra pure (E. Merck) tungstic acid 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 white. The thoroughly ground powder was taken in a silica dish and fired at a temperature in the range of 800-1100°C for an hour. The product was quenched in air. When the product attained the room temperature, it was pulverised and passed through a sieve of 300 mesh.

The relative spectral energy distribution of the phosphor powder was measured in the visible after

excitation with a monochromatic 2537 Å obtained from "HB0200" high pressure mercury discharge lamp (250 watts) using a Unicam SP 500 monochromator.

The fluorescence emission was measured in the visible with a Beckman Quartz spectrophotometer from 350 mμ to 600 mμ. The special distribution was compared with that of standard imported calcium tungstate phosphors.

The maximum intensity in the visible occurred at 440 mμ for all the phosphors. Our phosphor compared favourably with the imported ones in the intensity distribution.

A comparative study of the chromaticity of our phosphor with the imported ones gave the following results:

Phosphor	Dominant wavelength	Colour purity
(1) Our Phosphor	479 mμ	71.77%
(2) Imported (Japanese)	478.6 mμ	69.49%
(3) Imported (Derby)	483.5 mμ	56.3%

A comparison of the electron diffraction patterns showed that the crystal structures of the phosphors were identical.

#### Example II

Batch composition: Calcium carbonate: 80 g.  
Tungstic acid: 200 g.

The phosphor was prepared as in example I. The results of measurements were identical with those of Example I.

#### Example III

Batch composition: Calcium carbonate: 3 g.  
Tungstic acid: 7.5 g.

The phosphor was prepared as in Example I, excepting that the time of firing was about ½ hour. The results of measurements made were identical with those of Example I.

The following are among the main advantages of the invention:

(1) The blue phosphor which is entirely imported now can be produced indigenously.

Dated this 27th day of December, 1967.

Patents Officer,  
Council of Scientific & Industrial Research.

## COMPLETE SPECIFICATION

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJI 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 SURYA NARAYANA, Scientist, MOHAMMED IFTIKHAR AHMED SIDDIQI, Scientist, RAMAYYAR LAKSHMI NARAYANAN, Senior Scientific Assistant, NAGAMONY RAJARAM, Senior Scientific Assistant SABAPATHI BALACHANDRAN, Senior Scientific Assistant and RAMIAH KALYANASUNDARAM, Junior Scientific Assistant, all of the Central Electrochemical Research Institute, Karaikudi-3, Madras, India, all Indian citizens.

This invention relates to improvements in or relating to the preparation of calcium tungstate blue phosphor mainly used in fluorescent tube light industry.

Luminescent phosphors consist in general of a major proportion of a so-called base material or matrix and a minor proportion of another material called an activator or 'impurity'. Activators may act singly or in combination; in the latter case they may produce effects which are not obtainable when they are used singly in a given matrix material. A few materials both naturally occurring and synthetic are also known to give luminescence in pure state without requiring the use of any activator. In these cases 'defects' in the solid state naturally occurring or introduced during thermal treatment may act as activators. A substance which acts in a manner detrimental to luminescence in a given matrix is called 'a killer' and may be considered a negative activator. Since some activators may be effective in trace amounts, purity of materials used is of great significance.

The spectral energy distribution of emission of a phosphor when excited by a particular radiation depends on the matrix-activator composition. The intensity of emission depends on the processing conditions such as particle size, thermal treatment etc. A luminescent substance suitable for a particular use such as in the fluorescent tube lights should possess such desirable properties as high quantum efficiency i.e., high absorption of the ultraviolet radiation of 2537 Å and a high emission in the visible, stability during the tube manufacturing process and in subsequent performance when it is subjected to the presence of mercury discharge in the tube.

It has hitherto been known to prepare fluorescent material comprising calcium oxide and tungstic oxide, the calcium oxide being in excess of the amount required by the chemical formula  $\text{CaWO}_4$ .

Another hitherto known process for the preparation of luminescent tungstate materials comprise the step of prefiring a mixture of the oxide of the cation (or of each of the cations in the case of a mixed tungstate material) and tungstate oxide, or compounds yielding these oxides, at a temperature just sufficient for the formation of the desired tungstate and thereafter firing the prefired tungstate material in the usual way.

Exact detailed information on the method of making a luminescent material such as calcium tungstate is generally not available in the technical or patent literature. Even in the case of insufficiently reported methods of making the calcium tungstate blue phosphor, it has been considered necessary to do pre-heating and repeated heatings at higher temperature, which process is attended with uncertainties. Most of the luminescent phosphor including the blue calcium tungstate phosphor are, at present time almost completely imported from abroad.

The object of the present invention is to develop the know-how indigenously of the manufacture of luminescent calcium tungstate blue phosphor, particularly for use in fluorescent lamps or tubelights wherein the exciting radiation is the ultra-violet 2537 Å line of mercury, by a more straightforward method

which could be practised with precision and to characterize the luminescent calcium tungstate thus developed.

According to the present invention, the process for the production of luminescent calcium tungstate blue phosphor consists in making a slurry of a calcium oxide containing substance and a tungstic oxide-containing substance, the two oxides being in stoichiometric ratio, drying the slurry to and subsequently heating in the range of 800-1100°C to bring about a solid state reaction characterised in that the drying of the slurry is done by air drying to whiteness at 110°C whereby efficient calcium tungstate blue phosphor is obtained and the steps hitherto considered necessary of pre-heating and repeated heating at the high temperature are eliminated.

The process of making luminescent calcium tungstate blue phosphor thus comprises a step of pulverising together of a calcium oxide-containing material and a tungstic oxide-containing material and making a slurry of the mix with the addition of water, a second step of air-drying the slurry to whiteness at 110°C and a third step of subsequently heating the powdered substance in the air at a sufficiently high temperature for the formation of calcium tungstate, followed by quenching in air.

The luminescent calcium tungstate blue phosphor is characterised by the fact that when excited by 2537 Å it gives its emission in the visible range, the peak being at the blue wave-lengths.

The air-drying is done at about 110°C. The air-dried mass is white.

The high temperature used is in the range of 800-1100°C, but preferably about 1000°C.

The calcium oxide containing material and the tungstic oxide-containing material are used in such a proportion as to give the stoichiometric ratio of  $\text{CaO} : \text{WO}_3 : 1:1$ .

The calcium oxide-containing material and the tungstic oxide-containing material undergo decomposition on heating to high temperature so as to give the respective oxides namely calcium oxide ( $\text{CaO}$ ), and tungstic oxide ( $\text{WO}_3$ ) in a highly reactive form, and volatile products.

The calcium oxide-containing material may be calcium carbonate and the tungstic oxide-containing material may be tungstic acid.

The invention includes within its scope a fluorescent tube light incorporating a luminescent calcium tungstate blue phosphor made according to the invented method and composition.

Thus a solid state reaction is brought about between calcium oxide and tungstic oxide. A mixture is taken of a calcium oxide-containing substance such as calcium carbonate and a tungstic oxide-containing substance such as tungstic acid, both of a high degree of purity (given under examples) and in a finely divided state, in near stoichiometric ratio, a slurry is made with the addition of a suitable quantity of water, is dried at about 110°C, so that the resultant

ably with that of standard imported calcium tungstate blue phosphors. The maximum intensity in the visible that is the  $\lambda$  peak emission in the visible, occurred at 4000 m $\mu$  for all the phosphors. The characteristics of

the luminescent phosphors could be more fully and accurately described in terms of the following values resulting from a study of the chromaticity of our phosphor, as also the imported phosphors:

Table 1

Phosphor	Dominant wave-length	Colour co-ordinates		Colour
		X	Y	
1. CECRI Blue calcium tungstate phosphor	479.0 m $\mu$	0.1645	0.1845	71.77
2. Imported Japanese	478.6 m $\mu$	0.172	0.186	69.4
3. Imported Derby (U.K.)	483.5 m $\mu$	0.189	0.26	56.3

The colour point of our phosphor is indicated by point and white point by W in the chromaticity diagram (Fig. 4).

Based on the above measurements, it could be said that the efficiency of the luminescent calcium tungstate of this invention is quite high, comparable

with that of the imported ones, for in tubelights. Electron diffraction study has shown that the luminescent calcium tungstate of this invention has the crystalline structure of CaWO<sub>4</sub>. Table 2 compares the electron diffraction data on our phosphor with x-ray diffraction powder pattern for CaWO<sub>4</sub>.

Table 2

Electron diffraction pattern of calcium tungstate blue phosphor		X-ray diffraction powder pattern of CaWO <sub>4</sub> (Swanson Eg. A1. NBS circular No. 539, vol. 63 (1956).	
d(A)	I/I <sub>0</sub>	d(Å)	I/I <sub>0</sub>
4.731	w	4.76	53
3.119	s	{ 3.10	100
2.834	s	{ 3.072	31
2.598	w	2.844	14
2.268	m+	2.622	23
1.920	m+	{ 2.296	19
1.836	m	{ 2.256	3
1.692	w	2.0864	5
1.587	w	1.9951	13
1.443	m	1.9278	28
		1.8538	12
		1.7278	5
		1.6882	16
		1.6332	10
		1.5921	30
		1.5532	14
		1.4427	6

s = strong ; m=medium ;

w = weak

#### The main advantages of the invention:

These characteristics of the luminescent calcium tungstate blue phosphor resulting from this invention make it suitable for use in the low pressure mercury discharge fluorescent lamps. This phosphor when incorporated, in the manufacture of the commercial fluorescent tubelights of 2' and 4' length, has given satisfactory performance. It is stable in the manufacturing process and subsequent performance in actual use. It has a high efficiency. The luminescent calcium tungstate, in addition to its particular use in the fluorescent tubelights and other similar lamps based on the same principle, could have other uses such as in applications where the excitation is by electrons or x-rays. As a result of this invention, the luminescent calcium tungstate could thus be made indigenously. The invention relates to a straight forward process comprising of three main steps of pulverizing the raw materials and making a slurry air-drying at 110°C and heating at a high temperature in the range of 800-1100°C. In this invention the steps of pre-heating and re-heating at higher temperatures as reportedly used in the known methods, are not considered necessary. It could easily be practised on a commercial

scale requiring only simple and easily available equipment. In addition to making the know-how available indigenously, the immediate effect of this invention in practice would be a considerable saving in foreign exchange, as most of the phosphors are at present imported from abroad. The invention may also be helpful in earning foreign exchange by exporting the phosphor made indigenously or the fluorescent tubelights made from the same.

The invention thus makes available the know-how of making a luminescent calcium tungstate blue phosphor by a very much simplified and straightforward procedure. The invention consists essentially in making a slurry of a calcium oxide-containing substance and a tungstic oxide-containing substance, the two oxides being in stoichiometric ratio, air-drying the slurry at about 110°C to whiteness and subsequently heating at a high temperature in the range of 800-1100°C but preferably at about 1000°C, to bring about a solid state reaction between calcium oxide and tungstic oxide. It has been found that air-drying to whiteness at about 110°C is very vital to obtaining a good phosphor. The process does away with the steps of pre-heating and

repeated heatings at the higher temperature. The role of purity of the raw materials has been described. The fineness of particles used in the reaction being very important for getting efficient phosphors, this condition was ensured by taking the raw materials in a form which on decomposition at a high temperature leaves behind finely divided reactants. The luminescent calcium tungstate blue phosphor resulting from this invention has been characterised in terms of its crystal structure and chromaticity-

*We Claim*

1. A process for the production of luminescent calcium tungstate blue phosphor which consists in making a slurry of a calcium oxide-containing substance and a tungstic oxide containing substance, the two oxides being in stoichiometric ratio, drying the slurry and subsequently heating in the range of 800-1100°C to bring about a solid-state reaction characterised in that the drying of the slurry is done by air drying to whiteness at 110°C whereby efficient calcium tungstate blue phosphor is obtained and the steps hitherto considered necessary of pre-heating and repeated heating at the high temperature are eliminated.
2. A process as claimed in claim 1 which comprises a step of pulverizing together of a calcium oxide-containing material and a tungstic oxide-containing material and making a slurry of the mix with the addition of water, a second step of air-drying the slurry to whiteness and a third step of subsequently heating the powdered substance in air at a sufficiently high temperature for the formation of calcium tungstate, followed by quenching in air.
3. A process as claimed in claim 1 or 2 wherein the luminescent calcium tungstate blue phosphor is characterized by the fact that when excited by 2537Å, it gives its emission in the visible range, the peak being at the blue wavelengths.
4. A process as claimed in any of the preceding claims wherein the air-drying is done at about 110°C.
5. A process as claimed in any of the preceding claims wherein the air-dried mass is as nearly white as possible.
6. A process as claimed in any of the preceding claims wherein the high temperature used is in the range of 800-1100°C, but preferably about 1000°C.
7. A process as claimed in any of the preceding claims wherein the calcium oxide-containing material and the tungstic oxide-containing material are used in such a proportion as to give the stoichiometric ratio of CaO:WO<sub>3</sub>:1:1.
8. A process as claimed in any of the preceding claims wherein the calcium oxide-containing material and the tungstic oxide-containing material undergo decomposition on heating to high temperature so as to give the respective oxides namely calcium oxide (CaO), and tungstic oxide (WO<sub>3</sub>) in a highly reactive form, and volatile products.
9. A process as claimed in any of the preceding claims wherein the calcium oxide containing material is calcium carbonate and the tungstic oxide-containing material is tungstic acid.
10. A process of making calcium tungstate blue phosphor substantially as hereinbefore described.
11. A process of making calcium tungstate blue phosphor substantially as described in the examples.
12. A luminescent calcium tungstate blue phosphor whenever made by a method and of composition as claimed in claims 1-11.
13. A fluorescent tube light incorporating a luminescent calcium tungstate blue phosphor whenever made according to the method and of composition as claimed in claims 1-12.

Dated this 19th day of October, 1968.

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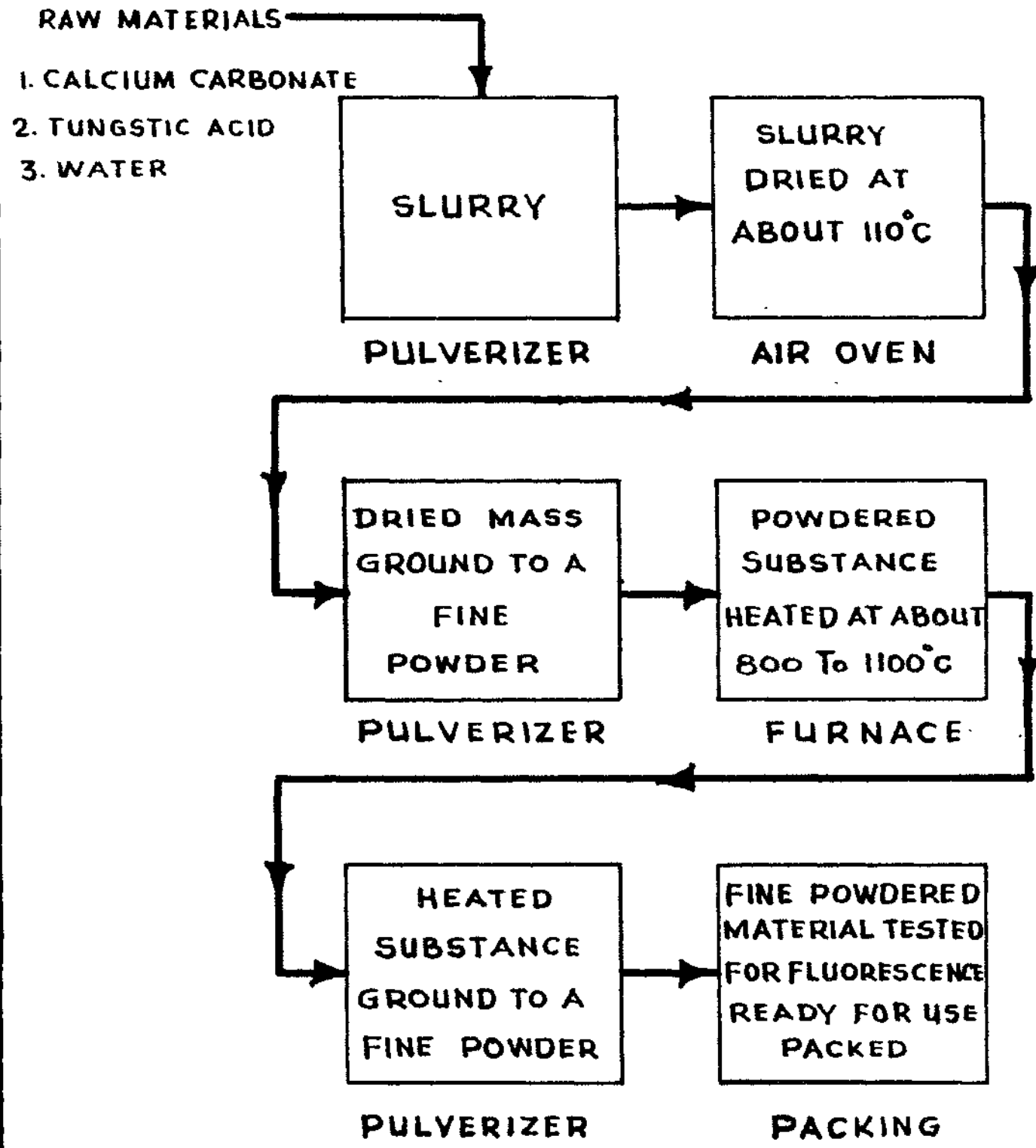


FIGURE-1

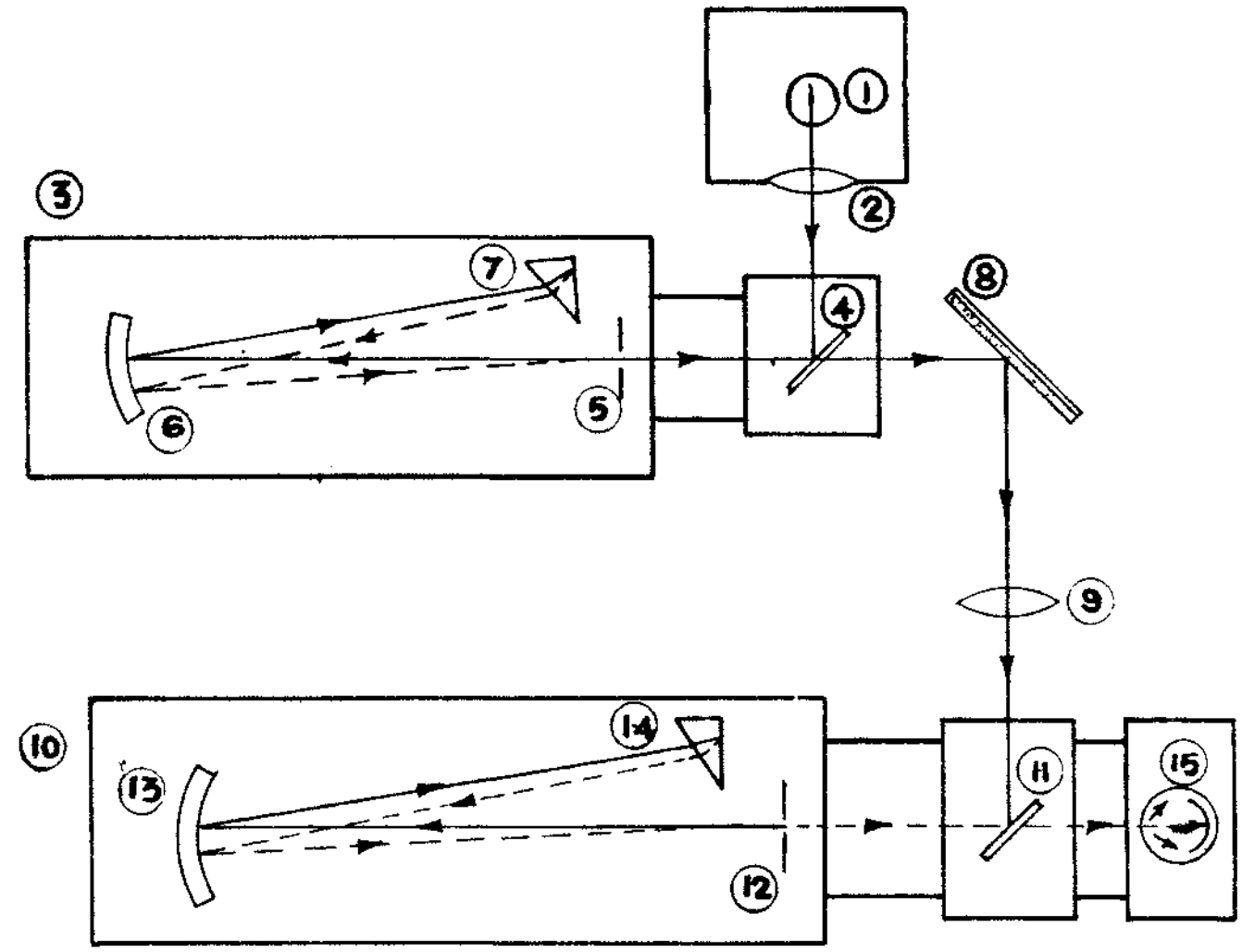


FIGURE-2

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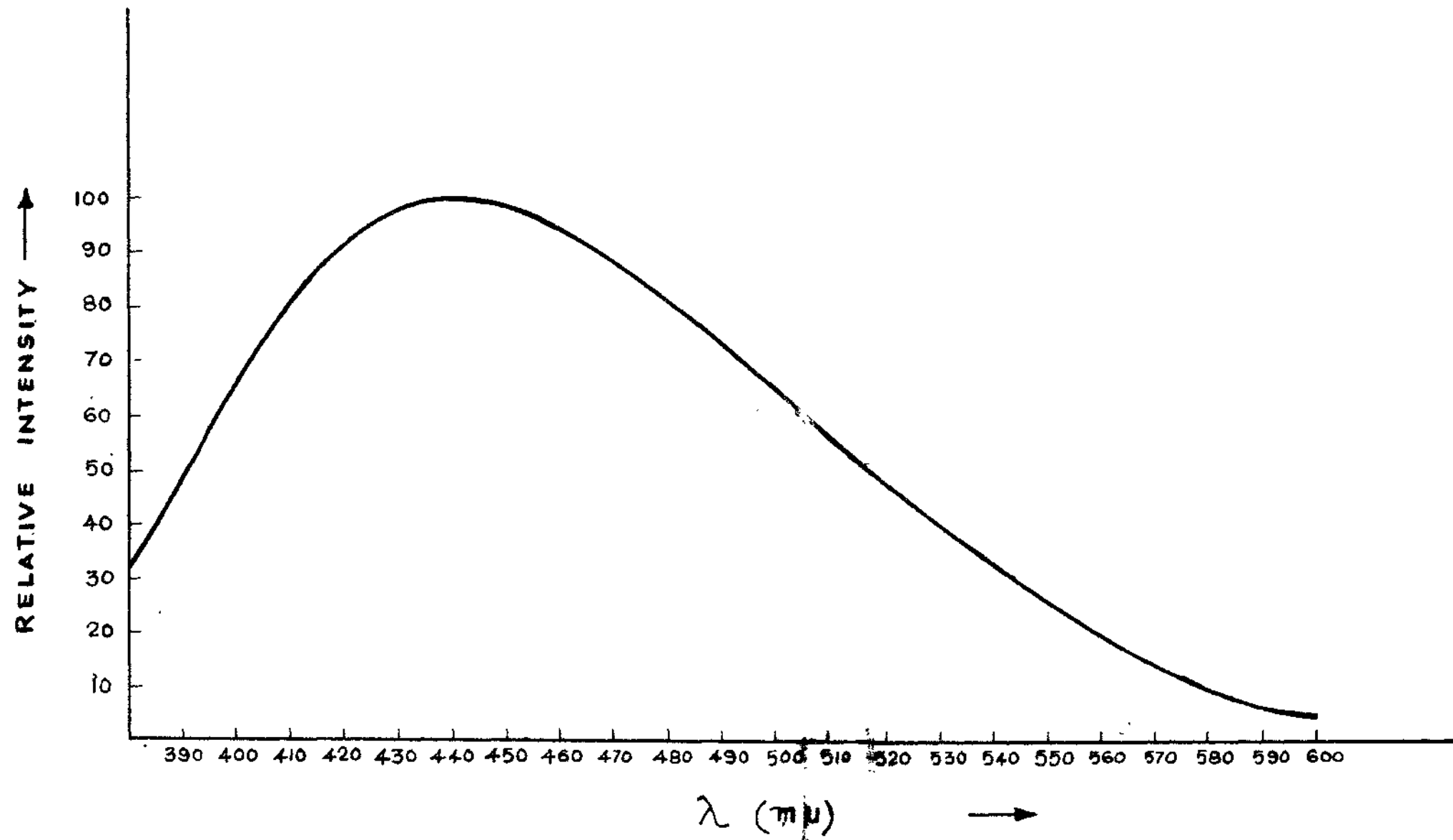


FIGURE-3

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COMPLETE  
SPECIFICATION

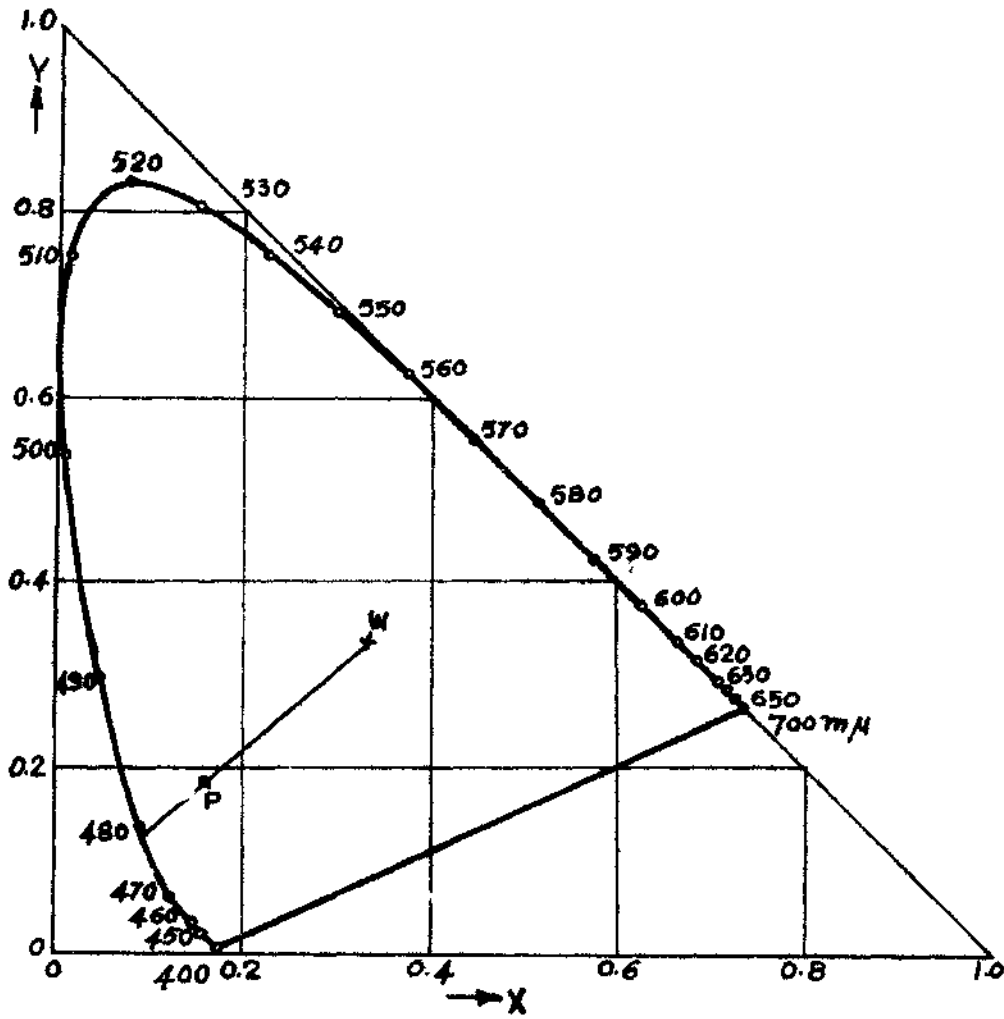


FIG-4

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