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Index at acceptance—121[LXIII(2)]

PROVISIONAL SPECIFICATION

“IMPROVEMENTS IN OR RELATING TO THE PREPARATION OF ZINC SILICATE GREEN PHOSPHOR”

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 :—

This is an invention by—

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This invention relates to improvements in or relating to the preparation of zinc silicate green phosphor particularly for use in fluorescent tube lights.

Zinc silicate (Willemite), the earliest known silicate for fluorescent purpose, when activated with about 0.2 — 2% Mn, gives green emission. However, this phosphor is at present imported.

In this background, the present invention provide with a straight forward method of making the zinc silicate green phosphor for use mainly in fluorescent tube lights, (low pressure mercury vapour discharge lamps), wherein the most predominant radiation is the 2537 Å line of the Hg. The zinc silicate green phosphor of our invention, when excited by 2537 Å, gives green emission, a comparatively narrow band concentrated in the wave length range 500-700 mμ, peaking at 530 mμ. The intensity of emission of our phosphor is equal to that of an imported green phosphor. The zinc silicate phosphor of our invention has an efficient absorption at 2537 Å. The phosphor also gives green emission on excitation by 3650 Å. Though the zinc silicate phosphor of our invention has been developed mainly for use in fluorescent tube lights, it could find other applications such as in oscilloscope screens, TV screens etc., either singly or in combination with other phosphors.

To these ends, the invention broadly consists of taking a mix of zinc oxide and silica, both of high purity, in a ratio preferably approximating to ZnO:SiO₂ :: 1:1, with a Mn content in the range of 1.0 to 2.5 % making a slurry with the addition of distilled water and subsequently heating the same in air, in fused (vitreous) silica crucibles, in the range of temperature 1100—1300°C, but preferably nearer the upper limit, for a time depending upon the quantity of the material, in order to obtain the solid-state reaction.

Any ZnO-containing material such as ZnCO₃ etc., and any SiO₂-containing material such as silicic acid, H₂SiO₃, could also be used with equally good results. Whereas the ZnO:SiO₂ ratio could theoretically be varied from 2:1 to 1:1 (it is reported that zinc orthosilicate is the only compound of ZnO and SiO₂ formed in all cases) we have found the optimum composition to be in the range of ZnO:SiO₂ :: 1.5 : 1.0 to 1:1 and, the manganese content to be 2% or 2.5% both being equally good.

Compositions close to 2:1 ratio of ZnO:SiO₂, always tend to be discoloured instead of pure white finished powders, giving very much lower intensity of emission. Temperature of heating lower than the optimum also has a similar effect.

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

Example 1

A batch composition comprising of :

ZnO = 0.81380 G (of BDH, AR grade)

SiO₂ = 0.60780 G (Natural quartz of high purity)

MnCl₂.4H₂O = 0.02878 G (of Derby Luminescents grade) was mixed and made into a slurry by grinding with the addition of a suitable quantity of distilled water. After it is dry, it is taken in a silica crucible and heated at a temperature around 1300° C for about 30 minutes. The product is quenched in air, and on obtaining the room temperature, is ground to a fine powder.

The spectral energy distribution of the phosphor powder was measured in the visible range from 350 mμ to 600 mμ with a Beckman quartz spectrophotometer on excitation by monochromatic 2537 Å, obtained from HBO 200 high pressure mercury discharge lamp (250 watts) using a UNICAM SP 500 monochromator.

The spectral energy distribution was compared with that of a standard imported green phosphor. The phosphor gives green emission, a comparatively narrow band concentrated in the wave length range 500—570 mμ, peaking at 530 mμ. The intensity of spectral energy distribution was equal to that of an imported green phosphor. The spectral energy distribution of our phosphor is given in Figure 1 of the accompanying drawings.

Example 2

A batch composition was used comprising of :

ZnO = 0.81380 g (of BDH, AR grade)

SiO₂ = 0.60780 g (Natural quartz of high purity)

MnCl₂.4H₂O = 0.03598 (Derby luminescent grade)

The phosphor was prepared as in example 1.

The results of measurement were identical with those of example 1.

The following are among the main advantages of our invention :

1. The invention provides with a straight forward method of making a zinc silicate green phosphor of high efficiency, mainly for use in fluorescent tube lights with clear-cut details.

2. The green phosphor which is imported at present could now be produced indigenously.

3. The zinc silicate green phosphor of our invention on excitation by 2537 \AA gives a green emission, a comparatively narrow band concentrated in the range 500—670 m μ peaking at 530 m μ .

Dated this 22nd day of October, 1971.

Sd.-

(R. BHASKAR PAI)

Patents Officer,

Council of Scientific and Industrial Research

COMPLETE SPECIFICATION

“IMPROVEMENTS IN OR RELATING TO THE PREPARATION OF ZINC SILICATE GREEN PHOSPHOR”

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, RAMAYYAR LAKSHMINARAYANAN, Senior, Scientific Assistant and VEDARAMAN SUNDARAM, Senior Laboratory Assistant, all of the Central Electrochemical Research Institute, Karaikudi-3 (S. Ry.), India, all Indian citizens.

This invention relates to improvements in or relating to the preparation of zinc silicate green phosphor particularly for use in fluorescent tube lights.

Luminescent phosphors consists, in general, of a major proportion of a so-called matrix material and a minor proportion of an ‘activator’ which could be an added ‘impurity’ or a ‘lattice defect’. Since certain impurities may act harmfully even 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 system and thermal history. Phosphors for fluorescent tube lights, should possess a high quantum efficiency *i.e.*, high absorption of the ultraviolet radiation of 2537 \AA and a high emission in the desired visible range, stability during the tube manufacturing process and subsequent performance.

Zinc silicate (Willemitte), the earliest known silicate for fluorescent purpose, when activated with about 0.22% Mn, gives green emission. However, this phosphor is at present imported. Some methods of making the phosphor reportedly incorporate manganese in a second heating at high temperature whereas other methods use more than one heating of the entire phosphor composition at high temperature. Moreover, a particularly interesting feature of the preparation of the zinc silicate phosphor pertains to the ZnO-SiO₂ phase diagram wherein the zinc orthosilicate Zn₂SiO₄ (or 2ZnO:SiO₂) is reported as the only compound stable in the binary system, this had led some workers to conclude that in phosphor preparation this compound alone is formed even if silica is initially in excess to composition, the excess silica then possibly going into solid solution.

It has been known that zinc silicates have the property of fluorescing with a green light. These materials have heretofore been prepared by heating together hydrated zinc oxide and hydrated silica in the proper chemical proportions to produce one of the zinc silicates ZnSiO₃ or Zn₂SiO₄. To this was also added a small percentage of an ‘exciter’ such as manganese chloride to put the material in a condition so that it will fluoresce.

It has been known that an improved green fluorescing materials may be made by heating together a zinc compound, such as zinc nitrate or zinc acetate which will fuse and decompose when heated in air to give zinc oxide at a temperature lower than that required to form the fluorescent material, silica, or a silicon compound, such as silicic acid, which will decompose when heated in air to give silica at a temperature lower than that required to form the fluorescent material and an exciter such as a manganese compound, preferably manganese dioxide or chloride or potassium permanganate. The proportions of the zinc compound and silica are preferably such that from one to twenty per cent, more zinc oxide is used than is required by the chemical formula ZnSiO₃. This produces a mixture which gives greater fluorescence when subjected to ultra violet radiations of 2537 angstroms than does the ordinary compound. The amount of manganese compound is calculated so that manganese is present in the quantity of 0.5 per cent to 3.5 per cent of the total weight. Mixtures of sixty parts ZnO forty parts SiO₂, and two parts of MnO₂, by weight, gave approximately five to fifteen per cent more light than ZnSiO₃ containing the same amount of manganese.

It is also known to make a coating of fluorescent material for an electric discharge lamp containing mercury vapour, the coating comprising a mixture of approximately by weight, 60 parts zinc oxide, 40 parts silica, 1.5 to 2.5 parts beryllium oxide, and a small quantity of an activator such as manganese dioxide or nitrate or to render the material luminescent. The coating is prepared by mixing 60 parts zinc oxide, 40 parts silica, 2 parts beryllium oxide, 4 parts manganese dioxide and 1/2 parts lithium chloride by weight the mixture being dried and fired, for example, at about 1,000° C for about three hours, or at about 1100° C for above a half hour, and the heated powder is then preferably quenched in water. The fluorescent colour of this material is a light yellow and may vary from pink to green with a change in proportion of the components. It should be noted that in this hitherto known process, it is not a zinc silicate phosphor at all which gives green luminescence but zinc beryllium silicate which does always give mainly a yellow colour and also green colour under some particular conditions and is now in disuse in view of its high toxicity. It is to get over this toxic effect that the calcium halophosphate daylight phosphor has been invented abroad.

In this background, the present invention provided a straightforward method of making the zinc silicate green phosphor for use mainly in fluorescent tube lights.

According to the present invention, there is provided a process for preparing a green phosphor used mainly

in fluorescent tube-lights wherein the exciting radiation is the UV 2537 Å and gives on excitation a green emission of a narrow band concentrated in the range 500—570 mμ, by the following steps, namely, (a) mixture of zinc oxide and silica of respective compounds which yield them on heating and manganese chloride or nitrate in ratio preferably approximating to ZnO : SiO₂ : : 1:1 with an Mn content in the range of 1.0 to 2.5% in finely divided form is made into a slurry with the addition of water, (b) the powdered mass is heated in silica vessel, (c) grinding and sieving the resulting product characterised in that the range of temperature of heating is in a narrow critical range between 1100° C to 1300° C preferably around 1250° C.

The duration of time is dependent upon the quantity of materials we take and the quantities of materials taken in the three examples given herein-below are such that the duration is about 30 minutes.

The zinc silicate green phosphor of our invention, when excited by 2537 Å gives green emission, a comparatively narrow band concentrated in the wave length range 500—570 mμ peaking at 530 mμ. The colour co-ordinates are as follows : x. 268, y 0.692, the colour purity is 91%, the predominant 5450 Å. The intensity of emission of our phosphor is equal to that of an imported green phosphor. The zinc silicate phosphor of our invention has an efficient absorption at 2537 Å. The phosphor also gives green emission on excitation by 3650 Å. Though the zinc silicate phosphor of our invention has been developed mainly for use in fluorescent tube lights, it could find other applications such as in oscilloscope screens, TV screens etc., either singly or in combination with other phosphors.

A mix of zinc oxide and silica, both of high purity is taken in a ratio preferably approximating to ZnO : SiO₂ : : 1:1, with a Mn content in the range of 1.0 to 2.5 % making a slurry with the addition of distilled water and subsequently heating the same in air, in closed fused (vitreous) silica crucibles, in the range of temperature 1100—1300° C, but preferably nearer the upper limit, for a time depending upon the quantity of the material, in order to obtain the solid-state reaction. In zinc silicate : Mn green phosphor, the manganese activator is known to be in the Mn²⁺ state.

Any ZnO-containing material such as ZnCO₃ etc., and any SiO₂-containing material such as silicic acid, H₂SiO₃ could also be used with equally good results. Whereas the ZnO : SiO₂ ratio could theoretically be varied from 2:1 to 1:1 (it is reported that zinc orthosilicate is the only compound of ZnO and SiO₂ formed in all cases), we have found the optimum composition to be in the range of ZnO : SiO₂ : : 1.5 : 1.0 to 1:1 and the manganese content to be 2% or 2.5, both being equally good. Manganese-containing compounds could be for instance chloride or nitrate.

Compositions close to 2:1 ratio of ZnO : SiO₂ always tend to be discoloured instead of pure white finished powders giving very much lower intensity of emission. Temperature of heating lower than the optimum also has a similar effect.

We have also studied the effect of each of the impurities Cd, Tl, Pb and Sb when added in a relatively small amount simultaneously with the Mn. The intensity of emission tends to decrease in that order, though the decrease is very slight for Cd. However, Cd in very trace amount may be beneficial from the point of view of stability of phosphor.

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

Example 1

A batch of composition comprising :

ZnO = 0.81380 g (of BDH, AR Grade)

SiO₂ = 0.60780 g (Natural quartz of high purity)

MnCl₂.4H₂O = 0.02878 g (of Derby luminescent grade)

was mixed and made into a slurry by grinding with the addition of a suitable quantity of distilled water. After it is dry, it is taken in a silica crucible and heated at a temperature around 1,300° C for about 30 minutes. The product is quenched in air and, on obtaining the room temperature is ground to a fine powder.

The spectral energy distribution of the phosphor powder was measured in the visible range from 350mμ to 600 mμ with a Beckman quartz spectrophotometer on excitation by monochromatic 2537 Å, obtained from HBO 200 high pressure mercury discharge lamp (250 watts) using a UNICAM SP 500 monochromator.

The spectral energy distribution was compared with that of a standard imported green phosphor. The phosphor gives green emission, a comparatively narrow band concentrated in the wave length range 500—570 mμ, peaking at 530 mμ. The intensity of spectral energy distribution was equal to that of an imported green phosphor. The spectral energy distribution of our phosphor is given in Figure 1 of the accompanying drawings. The colour co-ordinates are indicated in the chromaticity diagram of Figure 2.

Example 2

A batch of composition was used comprising :

ZnO = 0.81380 g (of BDH AR Grade)

SiO₂ = 0.60780 g (Natural quartz of high purity)

MnCl₂.4H₂O = 0.03598 g (Derby luminescent grade)

The phosphor was prepared as in example 1.

The results of measurement were identical with those of example 1.

Example 3

ZnO = 0.81380 g (BDH AR Grade)

SiO₂ = 0.60780 g (Natural quartz of high purity)

Mn (NO₃) 2.6HO₂ = 0.05267 g (BARC)

The phosphor was prepared as in example 1. The results of measurement were comparable with those of example 1. The following are among the main advantages of our invention :

The invention provides with a straightforward method of making a zinc silicate green phosphor of high efficiency, mainly for use in fluorescent tube lights with clear-cut details.

The green phosphor which is imported at present could now be produced indigenously.

The zinc silicate green phosphor of our invention on excitation by 2537 Å gives a green emission, a comparatively narrow band concentrated in the range 500—570 mμ peaking at 530 mμ.

WE CLAIM :

1. A process for preparing a green phosphor used mainly in fluorescent tube-lights wherein the exciting radiation is the UV 2537 Å, and gives on excitation a green emission of a narrow band concentrated in the range 500—570 mμ, by the following steps

namely, (a) mixture of zinc oxide and silica or respective compounds which yield them on heating and manganese chloride or nitrate, in ratio preferably approximating to $ZnO : SiO_2 :: 1:1$ with an Mn content in the range of 1.0 to 2.5% in finely divided form is made into a slurry with the addition of water, (b) the powdered mass is heated in silica vessel, (c) grinding and sieving the resulting product characterised in that temperature range of heating is in a narrow critical range between $1100^\circ C$ to $1300^\circ C$ preferably around $1250^\circ C$.

2. A process for preparing green phosphor used mainly in fluorescent tube lights substantially as hereinbefore described.

Dated this 15th day of November, 1972.

Sd.-

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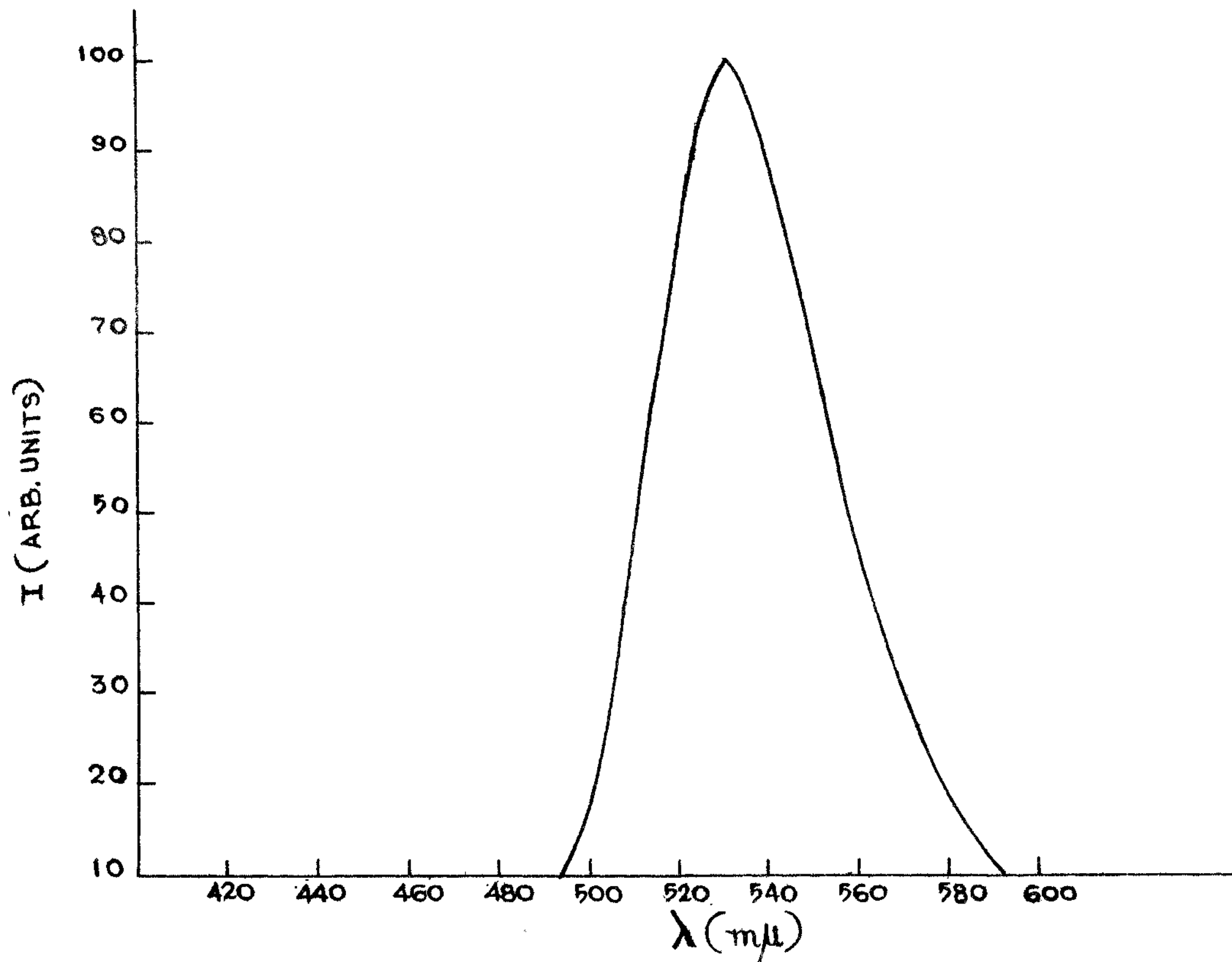


FIG. 1.

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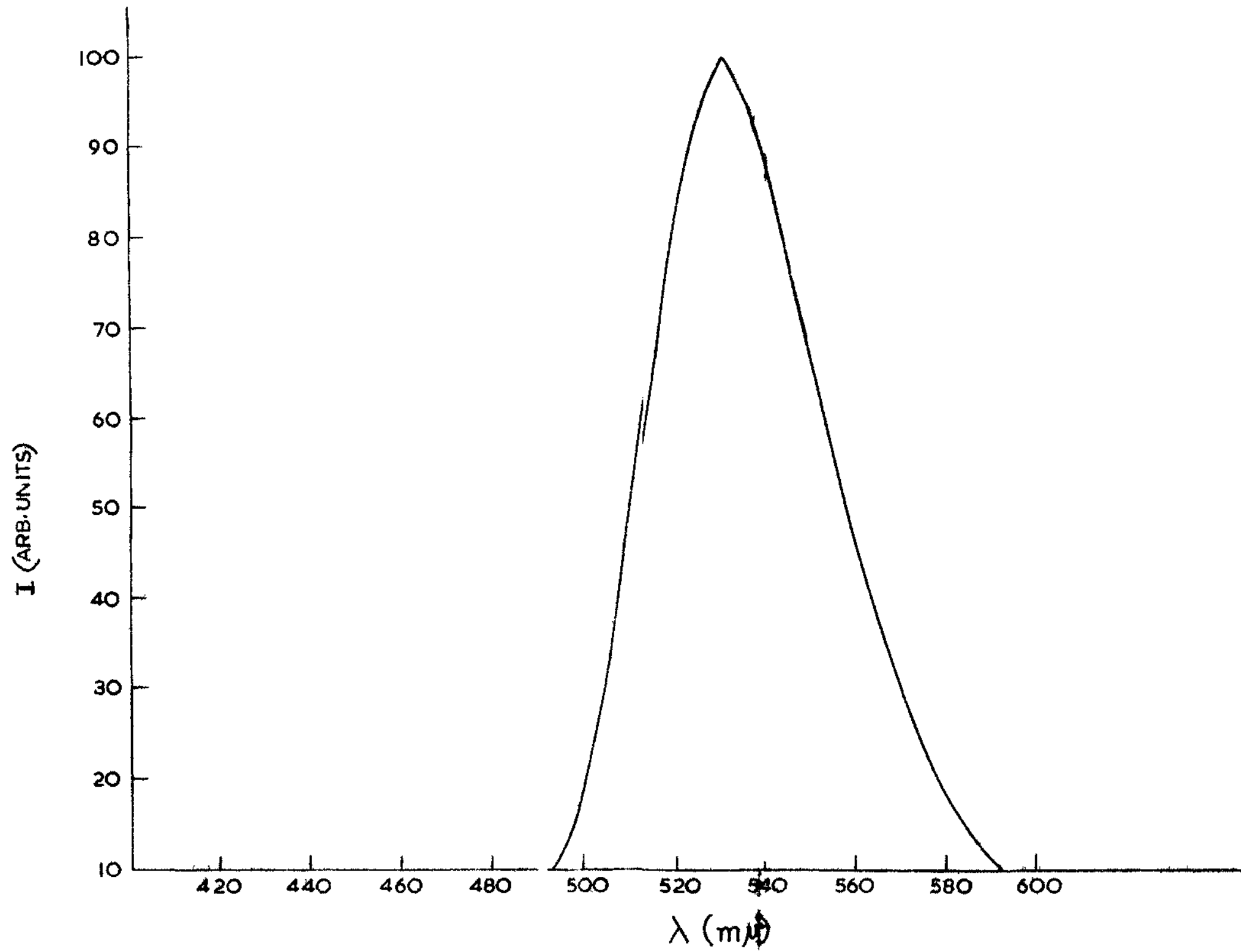


FIG. 1.

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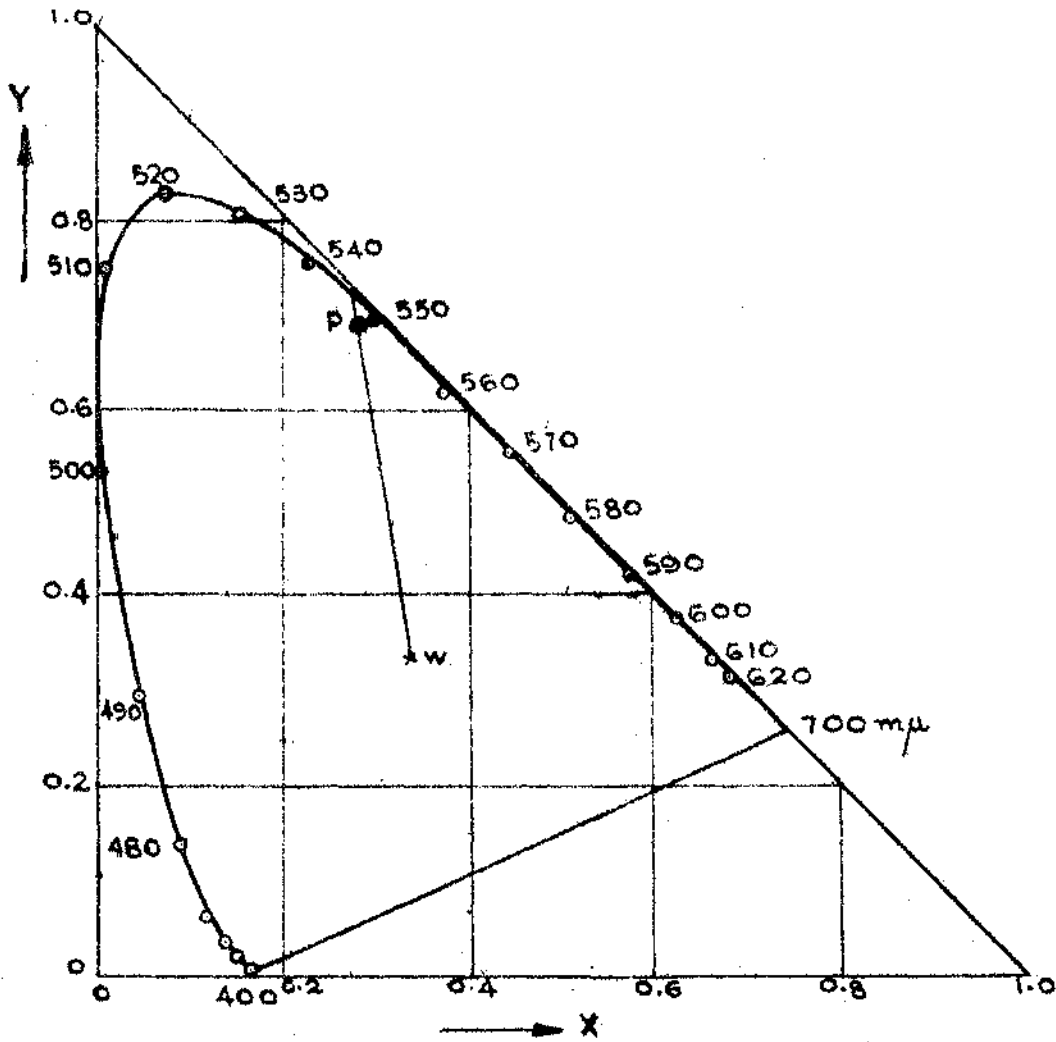


FIG. 2.

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