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PATENT SPECIFICATION

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Specification Accepted : Nov. 16, 1938.

PROVISIONAL SPECIFICATION
No. 10922 A.D. 1937.

Improvements in Combinations of a Source of Radiation with Material adapted to be Excited to Luminescence by the Radiation.

We, THE GENERAL ELECTRIC COMPANY LIMITED, of Magnet House, Kingsway, London, W.C.2, a British Company, and ALFRED HAMILTON MCKEAG and JOHN TURTON RANDALL, 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 combinations of sources of radiation with luminescent materials, that is to say, materials adapted to be excited to luminescence by the radiation from the source, exposed to the said radiation. Among the sources more especially concerned is an electric discharge emitting the mercury spectrum. When this is a low pressure discharge through the usual mixture of mercury and rare gas and the luminescent material is within the envelope, it is not certain that the only exciting agency is radiation; slow diffused electrons and metastable atoms may play some part. But any arrangement in which a material within an envelope is excited to luminescence by a discharge within the envelope is to be regarded as a combination of the kind to which the invention relates.

Among the luminescent materials that have been proposed in such combinations is cadmium phosphate activated by manganese. The use of this material in combination with a low pressure mercury discharge is described in Patent Number 469,731. The preferred method of preparing the material was to precipitate cadmium sulphate with ammonium phosphate, to add 0.1% of manganese, and to heat at a temperature of 1000° C. We have now discovered that a material of substantially different, and, in some combinations, more useful properties can be obtained by increasing the proportions of manganese very greatly, for example to 10%, and possibly modifying the heat treatment.

[*Price* 1*s.*]

The new material differs from the old in its crystalline form as indicated by its X-ray spacing. In the following table columns IIa and IIb give respectively, for the new material, the spacings in A.U. and the relative intensities on the usual arbitrary scale. The spacings of the old material are less easy to determine, since the number of lines in the same range is much greater and so numerous as to suggest that they do not all arise from a single crystal lattice. But 12 of the strongest lines have been measured in one sample of the old material; the corresponding spacings are given in column Ia; column Ib gives the intensities of these lines relative to each other, S meaning strong, M medium and W weak. But it is to be understood that there are many lines, which would ordinarily be called weak, much weaker than those marked W. The main purpose of columns I is to show that the new and old materials are clearly distinguishable.

I		II	
a	b	a	b
4.31	M	4.180	(5)
3.36	M	3.87	(5)
2.96	S	3.15	4
2.824	M	3.01	4
2.648	M	2.839	10
2.588	M	2.790	10
2.441	S	2.560	2
1.777	W	1.958	3
1.712	W	1.932	5
1.604	M	1.885	6
1.447	W	1.838	5
1.224	W	1.828	3
		1.775	5
		1.754	5
		1.614	4
		1.503	1
		1.486	1
		1.461	3
		1.434	3
		1.395	3
		1.265	2

As usual, some of the lines may be due to impurities; a number of spacings of weak lines have been omitted for both materials, but it will be evident to those skilled in the art that the list of spacings is sufficient to identify and to distinguish the two materials.

According to the invention in a combination of a source of radiation with luminescent material exposed to the radiation, a main constituent of the luminescent material is cadmium phosphate containing a proportion of manganese greatly exceeding 0.1% (and preferably of the order of 10%), the X-ray spacings of this material being substantially as set forth in columns IIa and IIb of the foregoing table.

One method of preparing luminescent material for a combination according to the invention will now be described by way of example.

A pure aqueous solution of cadmium sulphate and a pure aqueous solution of di-ammonium hydrogen phosphate are mixed in the proportions $3CdSO_4 : 2(NH_4)_2HPO_4$. The precipitated cadmium phosphate is mixed with enough manganese chloride in solution to give 10% Mn in the final product. The mixture is dried for 2 hours at about 200° C. and is then heated for one hour in air at 925° C.

The resultant material, as compared with that described in the said co-pending Application, gives orange rather than pink luminescent light and, when excited by that part of the mercury spectrum which passes through quartz, gives a higher efficiency. It is therefore suitable for use in combination with a high-pressure mercury-vapour discharge device having a quartz envelope, to add red light in which that source is deficient.

It can also be used on the interior surface of the envelope of a low-pressure mercury discharge. An efficiency of 30 lumen/watt with approximately white light can then be obtained by suitable adjustment, according to known principles, of the distribution of the material and the current density of the discharge.

Variations from the proportion of manganese and the heat treatment above described are permissible. But if the material containing 10% Mn is heated above 1000° C., the crystalline form given in columns Ia and Ib is apt to result, and the improved properties are not obtained. It is difficult by any heat treatment to obtain the crystalline form of columns II with less than 2% Mn; and if it is obtained, the luminescent properties are not as good as if the material contains 5—10% Mn. Proportions higher than 10% are permissible; no definite upper limit has been established.

Dated the 16th day of April, 1937.
For the Applicants,
NORMAN R. CAMPBELL.

PROVISIONAL SPECIFICATION
No. 1194 A.D. 1938.

Improvements in Luminescent Materials and in combinations therewith of Sources of Radiation adapted to Excite the Materials to Luminescence.

We, THE GENERAL ELECTRIC COMPANY LIMITED, of Magnet House, Kingsway, London, W.C.2, a British Company, and ALFRED HAMILTON MCKEAG, of Research Laboratories of The General Electric Company Limited, Wembley, Middlesex, and JOHN TURTON RANDALL, formerly of Research Laboratories of The General Electric Company Limited, Wembley, Middlesex, now of The University, Edgbaston, Birmingham, both British subjects, do hereby declare the nature of this invention to be as follows:—

This invention relates to materials of the type adapted to be excited to luminescence by aetherial radiation, or bombardment with charged particles or contact with an electric discharge through a gaseous medium, to the manufacture of such materials and to combinations of such materials with agencies adapted to excite them to luminescence.

In co-pending Application No. 10922/37 (Serial No. 495,706) a method of preparing such a material is described as follows. A pure aqueous solution of cadmium sulphate and a pure aqueous solution of di-ammonium hydrogen phosphate are mixed in the proportions $3CdSO_4$; $2(NH_4)_2HPO_4$. The precipitated cadmium phosphate is mixed with enough manganese chloride in solution to give 10% Mn in the final product. The mixture is dried for 2 hours at about 200° C. and is then heated for one hour in air at 925° C.

It is stated that the resulting material has certain advantages over the material described in Application No. 2535/36 (Serial No. 469,731), which is some kind

of cadmium phosphate containing only 0.1% Mn. In particular it gives orange rather than pink luminescent light and, when excited by that part of the mercury spectrum which passes through quartz, gives a higher efficiency. Columns IIa and IIb of a table in the said co-pending Application give the X-ray spacings of the resulting material. It is implied that the difference in the X-ray spacing and luminescent properties between the material of Application No. 10922/37 (Serial No. 495,706) and that of Patent Specification No. 469,731 lies in the larger manganese content of the former.

We have now discovered that this implication is false and that the difference arises from the larger content of chlorine which, in the said method of preparation, is introduced together with the manganese. If sufficient chlorine is introduced by some other method, for example by introducing some of the cadmium as chloride, the manganese content can be reduced as low as 0.5% without any great change in the luminescent properties of the resulting material. On the other hand it is remarkable that the presence of much larger amounts of manganese, for example 17.5% by weight of the element in the first product does no great harm.

The constitution of the material found in this manner has not been fully elucidated. On general chemical grounds it is probable that the main component of the material is one of the known chlor-phosphates, to which the formula $3Cd_3(PO_4)_2.CdCl_2$ is usually assigned. Further, the X-ray spacings given in the said columns IIa and IIb have been compared with those of the known lead chlor-phosphate to which the formula $3Pb_3(PO_4)_2.PbCl_2$ is usually assigned.

In R. W. G. Wyckoff's book, "The Structure of Crystals," page 300, this crystal is said to be hexagonal with a unit cell containing one molecule, having $a_0=10.03$ Å and $c_0=7.38$ Å, so that the axial ratio is 0.736. The X-ray spacings in the aforesaid columns IIa and IIb correspond closely to a hexagonal crystal with a unit cell having $a_0=9.67$ Å and $c_0=6.45$ Å, so that the axial ratio is 0.667. The crystals are therefore closely similar.

The X-ray spacings of material prepared according to the methods hereinafter described have been measured and the results shown in the following table have been obtained. The spacings do not seem to vary materially with the manganese content. It will be seen that this new table of spacings does not differ from the old by more than can be attributed to errors of measurement. The new table agrees better with the aforesaid crystal structure; accordingly the weak lines present in the old table, but not in the new, (i.e. those at 1.503, 1.486, 1.434) are probably due to impurities.

TABLE X.

INTERPLANAR SPACINGS FROM PATTERN OF CADMIUM CHLORO-PHOSPHATE 35P.

Spacing in A.U.	Intensity.
8.43	1
4.85	1
4.19	4
3.868	4
3.517	1
3.234	2
3.161	3
3.014	3
2.842	10
2.790	10
2.681	10
2.560	2
1.966	3
1.932	5
1.886	6
1.840	5
1.821	3
1.780	5
1.754	5
1.614	4
1.462	2
1.396	3

According to one aspect of the invention the manufacture of a luminescent material of the type specified comprises the step of inducing (for example by heat) a reaction in which all of the following reagents take part, namely, (1) a substance containing cadmium, (2) a substance containing chlorine, (3) a substance containing phosphorus combined with oxygen. As indicated above, the three reagents need not be all distinct. Thus they may be cadmium chloride, representing both (1) and (2), and cadmium phosphate, representing both (1) and (3). Further, reagents other than the said three may be present, and, in particular, a small amount of activator, which may be manganese, or a considerable amount of a manganese-containing substance which is neither (2) nor (3), for example manganese nitrate. But it appears to be undesirable that more than 25% of the material should consist of manganese.

According to another aspect of the invention, a luminescent material consists mainly or entirely of a crystalline substance to whose structure and luminescent properties all of the elements cadmium, manganese, chlorine, phosphorus and oxygen are essential. Other elements may

also be essential to the structure and/or luminescent properties.

Luminescent materials according to the second aspect of the invention or prepared according to the first aspect are adapted to be excited to luminescence by aetherial radiation of sufficiently short wavelength, which may however be capable of passing through quartz, or by contact with a gaseous medium through which an electric discharge passes, or by the incidence of cathode rays.

According to a third aspect of the invention means for producing light comprise a luminescent material according to the second aspect of the invention or prepared according to the first aspect associated with means for exposing it to one of the aforesaid agencies by which it is adapted to be excited to luminescence.

Two methods of preparing a luminescent material according to the invention will now be described by way of example; they are alternative to that described in the said copending application. The reagents used as the starting materials in these examples are all of the grade known under the trade name AnalaR grade. (AnalaR is a registered Trade Mark.)

Both methods contain a common step. In this step 480 gm. of cadmium sulphate is dissolved in 1500 ml. of distilled water, and 160 gm. of di-ammonium hydrogen orthophosphate is dissolved in 1000 ml. of boiling distilled water. 10 ml. of the second solution is added to the whole of the first; the precipitate formed is filtered off and discarded. The remainder of the second solution is added to the filtrate; the precipitate is filtered off, washed well with hot distilled water and dried at 180° C. for three hours. This precipitate, which is some form of cadmium phosphate, is called Precipitate A.

In the first method there is added to precipitate A 5% of its weight of manganese element in the form of a solution of manganous chloride in distilled water. A paste in which the precipitate and the solution are intimately mixed is formed, it is dried at 180° C. The product is ground and heated in air, in a tubular boat with one end closed by a glass wool plug, at 925° C. for half an hour.

In the second method, 370 gm. manganous sulphate are dissolved in 1500 ml. of boiling distilled water and 160 gm. di-ammonium hydrogen phosphate in 1000 ml. of boiling distilled water. The solutions are mixed and the precipitate formed is washed and dried at 180° C.; it is then precipitate B.

Precipitates A and B are mixed with solid cadmium chloride in the ratio of 100 parts of A to 20 parts of cadmium chloride to 5 parts of B. The substances are ground and thoroughly mixed together, the mixture is heated in a tubular boat, as before, to 800° C. for half an hour.

The material produced by either of these methods, when cold, emits orange-yellow luminescent light under excitation by radiation of wave-length between 2600 and 2000Å.

Dated the 13th day of January, 1938.
For the Applicants,
NORMAN R. CAMPBELL.

COMPLETE SPECIFICATION

Improvements in Luminescent Materials and in combinations therewith of Sources of Radiation adapted to Excite the Materials to Luminescence.

We, THE GENERAL ELECTRIC COMPANY LIMITED, of Magnet House, Kingsway, London, W.C.2, a British Company, and ALFRED HAMILTON MCKEAG, of Research Laboratories of The General Electric Company Limited, Wembley, Middlesex, and JOHN TUBTON RANDALL, formerly of Research Laboratories of the General Electric Company Limited, Wembley, Middlesex, now of The University, Edgbaston, Birmingham, 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, to methods of manufacturing them, and to means for producing light (more especially electric discharge lamps and cathode ray tubes) of which they form a part.

The narrower object of the invention is to provide a new luminescent material suitable for supplementing the light from mercury-vapour electric-discharge devices, so that the combination of the material and the device is a lamp which either is more efficient as a source of light than the device alone or emits a resultant radiation substantially different in colour from that of the device alone or both. When

a difference of colour is in view, it is usually desirable that the colour of the luminescent light should be "warm". Here and hereinafter the word "warm" means that the colour of the light departs from white in the direction of yellow or red and not in the direction of green or blue. But, as is well known, a material suitable for attaining this narrower object may be suitable for others; it is a wider object of the invention to produce a new luminescent material which is suitable for some purpose for which luminescent materials are at present used.

Luminescent materials are usually identified and distinguished from each other in a manner based on the work of Lenard and his school. They concluded that the essential components of a "phosphor" were a main component and an activator. The main component (here called the matrix) might be a chemical compound, such as ZnS, of definite stoichiometric composition; it might also be a solid solution of two such compounds, such as (Zn—Cd)S. The activator was an impurity, such as copper or silver or bismuth, embedded in the matrix, but, since there was no evidence of a stoichiometric ratio of matrix to impurity, not chemically combined with it. The quantity and colour of the luminescent light usually varied with the amount of the activator and with the heat treatment used in embedding it. But, since the range of colour with a given matrix and activator was not very large (it never, for example, extended from red to blue), all "phosphors" having the same matrix and the same activator, if luminescent at all, were regarded by Lenard, and have been regarded in the arts using luminescent materials, as the same luminescent material, although they might not have all the same luminescent properties.

Identification by matrix, defined by a chemical formula, and activator is not applicable to the new luminescent material about to be described. For in it the distinction between matrix and activator cannot be made with certainty for reasons hereinafter stated. It is necessary to find some method of identification which, while leading to the same associations and separations as the matrix-activator method among those materials to which that method is applicable, is also applicable to those materials in which the distinction between matrix and activator is not clear.

The new material will be identified by stating (1) the chemical elements essential to the material, (2) the crystal structure of the material as indicated by X-ray analysis, (3) the luminescent properties.

It must be understood that a material does not cease to be that described and claimed merely by being mixed with some other material, luminescent or non-luminescent, so long as the material retains in the mixture its characteristic crystal structure and luminescent properties. Again when a colour is prescribed for the luminescent light under a given excitation, it is not implied that the material cannot be excited otherwise or that, when it is excited otherwise, the colour of the luminescent light, is the same.

According to the invention a luminescent material (1) contains all of the elements cadmium and manganese and chlorine and phosphorus and oxygen, (2) is prepared by a process which produces in the finished product, a crystal structure in which the unit cell is hexagonal with axes substantially $a_0=9.7$ A.U. and $c_0=6.4$ A.U., and (3) is such that the finished product will emit under excitation by radiation of wave-length 2536 A.U. luminescent light whose colour is hereinbefore defined as warm. It is to be understood that these values of a_0 and c_0 refer to room temperature, say 18° C.

It is desirable to state the evidence on which the foregoing specification of the crystal structure is based. Table I below gives, in conventional manner, the direct results of an X-ray analysis of a sample of material prepared in the manner described hereinafter. Column 1 gives the quantity usually denoted by d/n for all lines observed, except a few so close to each other and/or so weak that they are difficult to measure; d/n is the spacing in A.U. between the atomic planes generating the observed lines on the assumption that all reflections are of the first order; Column 2 gives the intensities of the lines estimated visually. Column 3 gives the crystallographic indices of planes which would give the spacings in Column 1 if the lattice were hexagonal with $a_0=9.67$ and $c_0=6.45$; a numeral in brackets indicates, as usual, the order of reflection. (The notation adopted for the indices is that explained by A. W. Hull in the Physical Review, Vol. 17 (1921) p. 549). Within the range over which there are entries in Column 3, all possible spacings characteristic of this lattice are present, except those corresponding to planes 00.1 and 10.1. These should give spacings between the first and second row of the Table. Their absence is doubtless due to the fortuitous equivalence of different planes, such as is known to produce partial degeneracy of an X-ray pattern. In the range for which no entries are given in Column 3, there are several (often many)

alternative origins of the same spacing; it does not appear that any measured line is inconsistent with its arising from the said lattice.

TABLE I.

(1) d/n	(2) Intensity	(3) Planar indices.
8.43	1	10.0
4.85	1	11.0
4.19	3	10.0 (2)
3.87	3	11.1
3.52	1	20.1
3.23	1	00.1 (2)
3.16	2	12.0
3.01	3	10.2
2.842	6	12.1
2.790	6	10.0 (3)
2.681	6	11.2
2.560	2	10.1 (2) 30.1
1.966	2	
1.932	4	
1.886	5	
1.840	4	
1.821	3	
1.780	4	
1.754	4	
1.614	3	
1.503	1	
1.486	1	
1.462	2	
1.435	2	
1.396	2	
1.264	2	

Lines of appreciable strength other than those recorded have occasionally been found associated with the recorded lines. They have always been identified as lines appropriate to one of the starting materials from which the specimen was prepared, and especially to cadmium phosphate. Those skilled in the art will recognise that lines that can be attributed to an impurity likely to be present should always be excluded from any list intended to identify a lattice.

If Table I is compared with the Columns II of the table given in Provisional Specification No. 10922/37, (Serial No. 495,706) it will be seen that there is only one difference that cannot be attributed to experimental error or to a failure to record weak lines. This is the absence from the said specification of the spacing 2.681 A.U. It is not possible now to examine the cause of this discrepancy; for the specimen from which the previous table was derived is no longer available.

Measurements on other samples of the material have always given spacings differing from those of Table I (if at all) by amounts less than or scracely exceeding the experimental error, which may affect the second place of decimals, Accordingly in the foregoing statement of the invention, the second decimal place has been omitted.

We now proceed to methods of preparing the material, and therefore to the evidence for the component elements.

In every method by which we have actually prepared the material, a mixture is heated of which the components are a cadmium salt, a manganese salt, a chloride and an orthophosphate. (There are not always four components; the cadmium salt or the manganese salt may be a chloride or an orthophosphate). We have no evidence that it is possible to obtain a material which has both the aforesaid crystal structure (2) and the aforesaid luminescent property (3), unless it contains all of the elements cadmium and manganese and chlorine and phosphorus and oxygen. The proportion of manganese may be varied within wide limits without changing the crystal structure as revealed by X-ray analysis (it is possible that additional spacings characteristic of some other lattice may sometimes appear) or modifying substantially the luminescent properties. Further the acid radical of the manganese salt is not critical; the salt may be a chloride or phosphate, but it may also be, for example, a nitrate. It has not been found possible to prepare the material if metaphosphate is substituted for orthophosphate; but our experiments in this direction are not exhaustive; in particular the presence of deleterious impurities was not wholly excluded. In both the preferred method given below cadmium phosphate, obtained by precipitating a soluble cadmium salt with di-ammonium hydrogen orthophosphate, is one component of the mixture; but it need not be a component; the material has been prepared by heating together cadmium oxide, orthophosphoric acid (or phosphorus pentoxide), cadmium chloride and manganous phosphate. On the other hand no success could be obtained with one sample of cadmium phosphate, bought as pure; the products obtained with this material were highly coloured, and displayed no luminescence whatever; the material according to the invention is normally almost colourless.

These facts suggest at first sight that the material according to the invention consists essentially of a matrix of cadmium chlor-phosphate, of the composition generally written as $3Cd_3(PO_4)_2 . CdCl_2$, containing manganese as an activator. The failure to obtain the material with the said sample of cadmium phosphate may be due to a physical state of the sample which does not allow the man-

ganese to enter the lattice. Some confirmatory evidence is provided by the statement of R. W. G. Wyckoff in his book, The Structure of Crystals, (second edition) page 300 that lead chloro-phosphate, $3Pb_3(PO_4)_2.PbCl_2$, has a similar crystal lattice, namely hexagonal with $a_0 = 10.03$A.U., $C_0 = 7.38$A.U. (Wyckoff does not mention a cadmium chloro-phosphate).

On the other hand, it does not appear necessary that the chlorine content of the material should be that indicated by the said suggested formula (namely 4.02% Cl). Good results have been attained when the amount of chlorine originally added is considerably less than this. Thus, in the first method of preparation described hereinafter, the proportion added is only 2.8%; and even when, as in the second method described hereinafter, the chlorine added exceeds 4.02%, less than this amount is usually found in the material after water-soluble (and therefore presumably unchanged) chloride has been removed from it. Again, if the manganese is a mere activator, the permissible variation in the activator is much wider than usual; materials of substantially the same luminescent properties have been prepared containing as little as 1% or as much as 20% of the element manganese; it is not certain that even these wide limits may not be exceeded. A weak luminescence has been found with as little as 0.01% manganese; but it is possible that the material should then be regarded as a mixture of luminescent and inert material. The possibility that part of the manganese may replace cadmium isomorphously in the lattice cannot be ignored; but this would not by itself explain the deficiency in chlorine, even when X-ray analysis shows little or no excess of cadmium phosphate.

Two alternative methods of preparing material according to the invention will be described in detail; the second of them appears to be slightly preferable, and to give on the average rather higher efficiencies. The reagents other than cadmium chloride used as the starting materials in these methods are all of the kind known under the trade name AnalaR grade. (AnalaR is a registered trade mark.) Cadmium chloride is not available in this grade; ordinary commercial material was used. Both methods contain a common step. In this step 480 gm. of cadmium sulphate is dissolved in 1500 ml. of boiling distilled water, and 160 gm. of di-ammonium hydrogen orthophosphate is dissolved in 1000 ml. of boiling distilled water. 10 ml. of the second solution is added to the whole of the first; the precipitate formed is filtered off and discarded. The remainder of the second solution is added to the filtrate; the precipitate is filtered off, washed well with hot distilled water, and dried at 180° C. for three hours. This precipitate, which is some kind of cadmium phosphate, is called Precipitate A.

In the first method there is added to precipitate A 5% of its weight of manganese element in the form of a solution of manganous chloride in distilled water. A paste in which the precipitate and the solution are intimately mixed is formed; it is dried at 180° C. The product is ground and heated in air, in a tubular boat with one end closed by a glass wool plug, at 925° C. for half an hour. The resulting material is washed by decantation with hot distilled water six times, and dried at 180° C. for 2 hours.

In the second method, 370 gm. manganous sulphate are dissolved in 1500 ml. of boiling distilled water and 160 gm. di-ammonium hydrogen phosphate in 1000 ml. of boiling distilled water. The solutions are mixed and the precipitate formed is washed and dried at 180° C.; it is then precipitate B.

Precipitates A and B are mixed with solid cadmium chloride in the ratio of 100 parts by weight of A to 20 parts of cadmium chloride to 5 parts of B. The substances are ground and thoroughly mixed together, the mixture is heated in a tubular boat, as before, to 800° C. for half an hour. The resulting material is washed and dried as in the first method.

We have made extensive experiments, and have found no better method of preparation than the two simple ones just described; but analogy with other luminescent materials suggests that manufacture will be improved continually as experience is gained, or by definite modifications of the methods.

The material produced by either of these methods emits luminescent light, of a colour ranging from orange-yellow to pink, with a useful efficiency under excitation by any radiation with a wavelength within the range 2200—2600 A.U., which includes the mercury resonance line at 2536 A.U.; the efficiency of luminescence under radiation of wavelength as long as 3650 A.U. (another strong mercury line) is considerably less, but appears to increase with the content of manganese. Excitation by radiation of wave-length less than 2000 A.U. has not been examined fully owing to experimental difficulties; but it does not appear that the material is likely to be usefully associated with the neon discharge in the manner described in Patent Specification

No. 457,486, if only because the colour of the luminescent light is not very different from that of the light from neon. When bombarded by electrons having an energy of some 6000 electron-volts, the material emits luminescent light of a colour rather yellower than that emitted under excitation by 2536 A.U. Thus the material may be used for the fluorescent screens of cathode-ray tubes; but, if a less highly coloured light is required (as is usual), it must be mixed in known manner with some material emitting greener or bluer light, for example willemite.

The most important use for the material discovered so far is that indicated by the narrower object of the invention. Since the luminescent material is excited by that part of the mercury spectrum that is transmitted by quartz, it may be usefully combined with a high-pressure mercury-vapour discharge lamp having a quartz envelope to increase the red content of the total light. The material should then, of course, be placed outside the envelope. It may be mixed in known manner with other luminescent materials and, in particular, with those that add blue light of suitable colour. The term "mercury" does not imply the absence of substances, additional to mercury, which may contribute appreciably to the light from the lamp.

The material can also be used on the interior surface of a low pressure mercury discharge lamp. If it is distributed uniformly (except possibly at the ends) in a layer of suitable thickness, and the current density of the discharge is some 20 mA/cm^2, an overall efficiency of 25 lumen/watt can be obtained, the colour of the resultant light being a very pale pink.

We are aware of Patent Specification No. 473,715, which relates to the preparation of phosphorescent material by heating zinc sulphide or mixed crystals of zinc and cadmium sulphide together with a flux. Among the materials that may be used as a flux there are mentioned chlorides, manganese compounds and tertiary sodium phosphate; but we are not aware that it is proposed to include in the same flux all of the three substances chlorine, manganese and a phosphate. Neither zinc nor sulphur is an essential constituent of material according to the invention; and no benefit is known to be derived from the presence in such material of either of these two elements.

We are aware that Patent Specification No. 469,731, published after the date of this application claims:—

1. A source of approximately white light of the type specified wherein the said luminescent material is cadmium phosphate having substantially the gravimetric composition of the material prepared by one or other of the two methods aforesaid and activated so that it emits reddish luminescent light and has otherwise substantially the luminescent properties of the material prepared by the said methods, and the proportion of the primary radiation from the mercury spectrum to the secondary radiation from the cadmium phosphate is so adjusted that the efficiency is approximately a maximum.

2. A source of light according to Claim 1, wherein phosphoric acid is used as the binder for attaching the luminescent material to its support.

3. The method of manufacturing a source of light according to Claim 1 or 2, wherein the said luminescent material is prepared by precipitating cadmium sulphate with ammonium phosphate and adding manganese as an activator, substantially as hereinbefore described by way of example.

We are aware also that it is proposed in the said Specification to introduce the manganese, added as activator, in the form of manganese chloride.

As indicated in Provisional Specification No. 10922/37, (Serial No. 495,706) our experiments indicate that material prepared by either of the methods described in the said Specification No. 469,371 has not the crystal structure characteristic of luminescent material according to the present invention.

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. A luminescent material which contains all of the elements cadmium and manganese and chlorine and phosphorus and oxygen, prepared by a process which produces in the finished product a crystal structure wherein the unit cell is hexagonal and has axes substantially $a_0=9.7$ A.U. and $C_0=6.4$ A.U., and which is such that the finished product will emit under excitation by radiation of wavelength 2536 A.U. luminescent light whose colour is hereinbefore defined as warm.

2. The method of manufacturing a luminescent material according to Claim 1 which comprises the step of heating together a mixture of components which components include a cadmium salt, a manganese salt, a chloride, and an orthophosphate (or ortho-phosphoric acid or phosphorus pentoxide).

3. A luminescent material prepared substantially by one of the two methods hereinbefore described in detail.

No. 457,486, if only because the colour of the luminescent light is not very different from that of the light from neon. When bombarded by electrons having an energy of some 6000 electron-volts, the material emits luminescent light of a colour rather yellower than that emitted under excitation by 2536 A.U. Thus the material may be used for the fluorescent screens of cathode-ray tubes; but, if a less highly coloured light is required (as is usual), it must be mixed in known manner with some material emitting greener or bluer light, for example willemite.

The most important use for the material discovered so far is that indicated by the narrower object of the invention. Since the luminescent material is excited by that part of the mercury spectrum that is transmitted by quartz, it may be usefully combined with a high-pressure mercury-vapour discharge lamp having a quartz envelope to increase the red content of the total light. The material should then, of course, be placed outside the envelope. It may be mixed in known manner with other luminescent materials and, in particular, with those that add blue light of suitable colour. The term "mercury" does not imply the absence of substances, additional to mercury, which may contribute appreciably to the light from the lamp.

The material can also be used on the interior surface of a low pressure mercury discharge lamp. If it is distributed uniformly (except possibly at the ends) in a layer of suitable thickness, and the current density of the discharge is some 20 mA/cm^2, an overall efficiency of 25 lumen/watt can be obtained, the colour of the resultant light being a very pale pink.

We are aware of Patent Specification No. 473,715, which relates to the preparation of phosphorescent material by heating zinc sulphide or mixed crystals of zinc and cadmium sulphide together with a flux. Among the materials that may be used as a flux there are mentioned chlorides, manganese compounds and tertiary sodium phosphate; but we are not aware that it is proposed to include in the same flux all of the three substances chlorine, manganese and a phosphate. Neither zinc nor sulphur is an essential constituent of material according to the invention; and no benefit is known to be derived from the presence in such material of either of these two elements.

We are aware that Patent Specification No. 469,731, published after the date of this application claims:—

1. A source of approximately white light of the type specified wherein the said luminescent material is cadmium phosphate having substantially the gravimetric composition of the material prepared by one or other of the two methods aforesaid and activated so that it emits reddish luminescent light and has otherwise substantially the luminescent properties of the material prepared by the said methods, and the proportion of the primary radiation from the mercury spectrum to the secondary radiation from the cadmium phosphate is so adjusted that the efficiency is approximately a maximum.

2. A source of light according to Claim 1, wherein phosphoric acid is used as the binder for attaching the luminescent material to its support.

3. The method of manufacturing a source of light according to Claim 1 or 2, wherein the said luminescent material is prepared by precipitating cadmium sulphate with ammonium phosphate and adding manganese as an activator, substantially as hereinbefore described by way of example.

We are aware also that it is proposed in the said Specification to introduce the manganese, added as activator, in the form of manganese chloride.

As indicated in Provisional Specification No. 10922/37, (Serial No. 495,706) our experiments indicate that material prepared by either of the methods described in the said Specification No. 469,371 has not the crystal structure characteristic of luminescent material according to the present invention.

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. A luminescent material which contains all of the elements cadmium and manganese and chlorine and phosphorus and oxygen, prepared by a process which produces in the finished product a crystal structure wherein the unit cell is hexagonal and has axes substantially $a_0 = 9.7$ A.U. and $C_0 = 6.4$ A.U., and which is such that the finished product will emit under excitation by radiation of wavelength 2536 A.U. luminescent light whose colour is hereinbefore defined as warm.

2. The method of manufacturing a luminescent material according to Claim 1 which comprises the step of heating together a mixture of components which components include a cadmium salt, a manganese salt, a chloride, and an ortho-phosphate (or ortho-phosphoric acid or phosphorus pentoxide).

3. A luminescent material prepared substantially by one of the two methods hereinbefore described in detail.

4. Means for producing light comprising a combination of luminescent material with means adapted in operation to excite it to luminescence wherein the said luminescent material (1) contains all of the elements cadmium and manganese and chlorine and phosphorus and oxygen, (2) has a crystal structure in which the unit cell is hexagonal with axes substantially $a_0 = 9.7$ A.U. and $c_0 = 6.4$ A.U. and (3) emits under excitation by radiation of wave-length 2536 A.U. luminescent light whose colour is hereinbefore defined as warm.

5. Means for producing light comprising a combination of luminescent material with means adapted in operation to excite it to luminescence wherein part at least of the said luminescent material has been manufactured according to Claim 2.

6. Means for producing light comprising a combination of luminescent material with means adapted in operation to excite it to luminescence wherein part at least of the said luminescent material has been prepared substantially according to one of the two methods hereinbefore described in detail.

7. Means according to Claim 4, 5 or 6 wherein the said exciting means is a high-pressure mercury-vapour discharge lamp with a quartz envelope.

8. Means according to Claim 4, 5 or 6 wherein the said exciting means is a low-pressure mercury vapour discharge device and wherein the luminescent material is within the envelope of the said device.

9. Means according to Claim 4, wherein the said exciting means is a cathode-ray tube and wherein the said luminescent material is part or the whole of the fluorescent screen of the said cathode ray tube.

Dated the 17th day of February, 1938.
NORMAN R. CAMPBELL,
For the Applicants.

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