

[54] **ELECTRICAL TRANSLATING DEVICE
CONTAINING SPHEROIDAL
PHOSPHORS**

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[22] Filed: **July 1, 1968**

[21] Appl. No.: **741,717**

[52] U.S. Cl. **313/109, 117/33.5, 252/301.4, 313/92**

[51] Int. Cl. **H01j 1/63, H01j 63/04**

[58] Field of Search **313/109, 92, 108; 252/301.4, 252/301.2, 301.3, 301.5, 301.6; 117/33.5**

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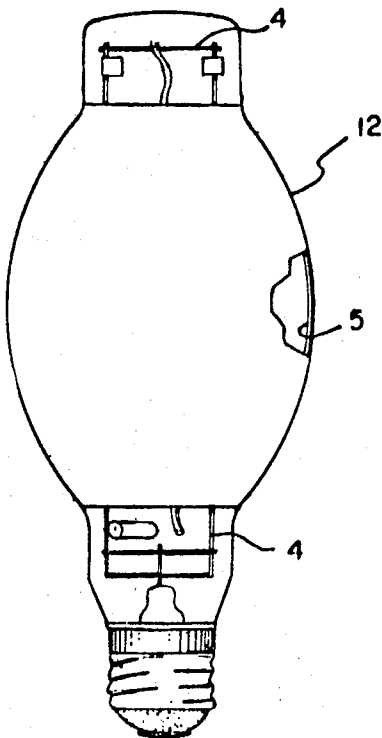
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[57] **ABSTRACT**

A fluorescent lamp with an inorganic phosphor coating on the lamp envelope. The phosphor particles have the shape of foraminous spheres with a diameter between about 3 and 20 μ . In the preferred embodiment, these spheres are hollow so that there is a maximum of emitting surface for a minimum weight of powder.

12 Claims, 4 Drawing Figures



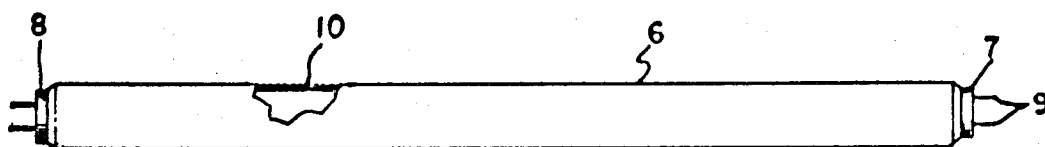


FIG. 1

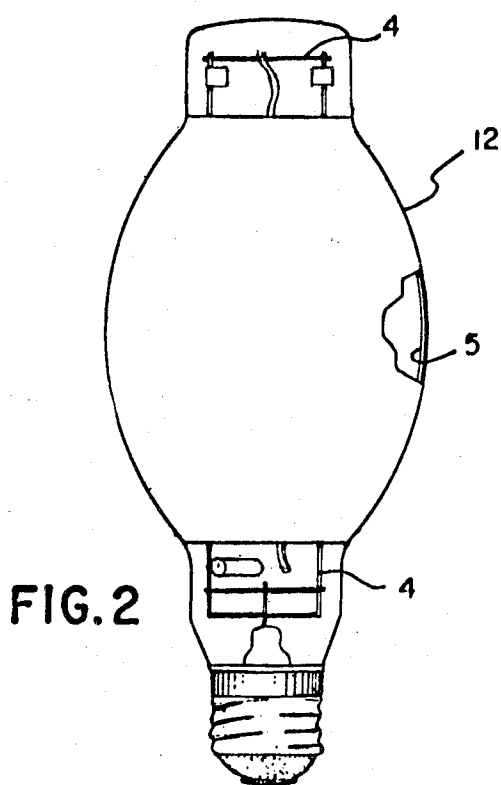


FIG. 2

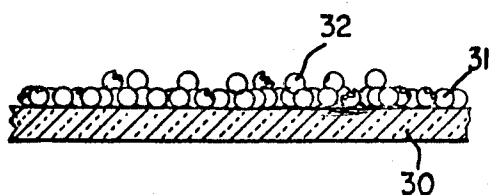


FIG. 3

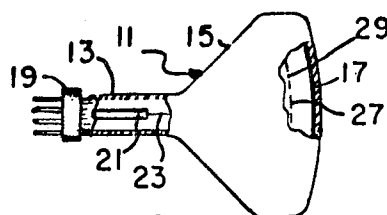


FIG. 4

ELECTRICAL TRANSLATING DEVICE CONTAINING SPHEROIDAL PHOSPHORS

BACKGROUND OF THE INVENTION 1. Field of the Invention

This invention relates to electrical translating devices and particularly to lamps and cathode ray tubes which have spherically shaped phosphors disposed upon the internal surfaces thereof. The lamps may be either the fluorescent-type where a low pressure mercury arc directly impinges against the phosphor or the high pressure mercury-type where ultraviolet radiation is emitted from an arc tube which, in turn, energizes the phosphor. The cathode ray tubes operate when cathode rays impinge upon the phosphor.

2. Description of the Prior Art

Fluorescent materials which have been used in electrical translating devices have generally been crystalline powders. They were disposed upon the envelope so as to absorb the maximum amount of ultraviolet light or incident cathode rays. The particles had irregular shapes, as is common in crystalline materials, and they varied widely in size. For optimum performance in lamps, particles less than 3μ , generally called superfines, had to be removed because they scattered the ultraviolet light instead of making it available for absorption. On the other hand, the very large particles, greater than about 20μ , produced a grainy appearance on the lamp. They were so large that the surfaces of the individual abutting particles left large voids between them.

SUMMARY OF THE INVENTION

According to the present invention, we have discovered that spherically shaped phosphors, preferably porous, can be made and such materials can emit substantially more light per unit weight than was obtainable heretofore. In accordance with a preferred embodiment, the phosphor spheres are hollow, thereby enabling any ultraviolet light which penetrates the shell to excite emission also, thereby effectively giving more than one emitting surface. In many cases, the shells of these hollow spheres break and the ultraviolet light can easily reach both the inside and the outside. The spheres preferably have a diameter between about 3 and 20μ and when they are hollow, a wall thickness between about 0.5 and 8μ .

Such phosphor spheres can be disposed upon the envelope surface according to techniques which are conventional in the lamp and cathode-ray tube art. For example, for lamps, the phosphor is dispersed in an ethyl cellulose binder and coated upon the bulb wall. The binder is then baked off and the phosphor spheres are left coated upon the wall.

DESCRIPTION OF THE DRAWING

FIG. 1 is a perspective view, partially broken away, of a fluorescent lamp utilizing spheroidal phosphors.

FIG. 2 is a perspective view, partially broken away, of a high pressure electric discharge device utilizing the same phosphor.

FIG. 3 is a perspective view, partially broken away, of a cathode ray tube with the spheroidal phosphors upon the screen.

FIG. 4 is a section of a glass wall showing the disposition of spheroidally shaped phosphors.

Referring now to FIG. 1, a typical fluorescent lamp containing mercury vapor is shown including a glass envelope 6 having end caps 7 and 8 with electrical lead-in wires 9 and connected to cathodes (not shown). A layer 10 of spheroidal phosphor is coated upon the internal surface of the glass envelope 6.

Referring now to FIG. 2, the high pressure mercury lamp is shown which includes the conventional arrangement of an arc tube (not shown) supported upon the metal harness 4. Surrounding the arc tube and harness is a bulbous envelope 12, with a coating 5 of the spheroidal phosphor of our invention disposed upon the internal surfaces thereof.

The spheroidal phosphor of our invention can be disposed upon the screen of a cathode ray tube such as shown in FIG. 3

and commonly in use in television receiving apparatus. The tube comprises an envelope 11 having a neck portion 13, a funnel portion 15, and a face panel 17. A tube base 19 is attached to the neck portion 13 to provide means for connecting the tube electrodes with their associated receiver circuitry. Within the neck 13 there is mounted an electron gun or guns 21 which provide the electron beam or beams 23 utilized in the operation of the tube. A color screen 25 having the usual configurations of color-emitting phosphor is formed on the internal surface of face panel 17. Positioned adjacent to screen 25, but substantially spaced therefrom, is a mask or grid 27 having therein a plurality of apertures 29. The type of tube illustrated in FIG. 4 may use grid 27 primarily to either focus or deflect beam 23, or to mask, or to mask and focus the electron beam to attain proper electron impingement upon the color screen 25. The specific grid and screen structures and the potentials on the grid and screen will determine the type of operation in a manner well understood in the art.

In FIG. 3, a glass surface 30 is shown with a plurality of porous spheres 31 of phosphor disposed thereon. The surface 30 can be from any of the broken-away sections of FIGS. 1, 2 or 3. The spheres are preferably arranged so that they abut against the glass and also against each other so as to form a uniform layer. Some of the spheres 32 can be disposed on top of the spheres 31 which are abutting against the glass surface 30. In some cases it may even be highly desirable to have several of the spheres stacked one upon the other so as to avoid the possibility that some of the energizing radiation may miss the phosphor.

As shown, the spheres are hollow, which is the preferred embodiment. Hollow spheres can be lighter than solid ones and hence coating weight can be reduced. With hollow spheres, many may be cracked or broken and thus the internal surfaces are exposed to the exciting radiation also. On the other hand, because the spheres are porous, exciting radiation which is produced in the device can penetrate the phosphor through the foramina and excite the internal surfaces.

Spheroidal phosphors can be prepared by mixing solutions of materials necessary to form such phosphors, in the appropriate quantities, and then atomizing the solution in a heated gaseous stream, such as disclosed in the copending application of Dale et al., Ser. No. 606,159, filed Dec. 30, 1966 and assigned to the assignee of the present invention.

When using the spray-dry techniques for preparing the spheroidal phosphors, all of the materials necessary for their formation are dissolved and a solution of the admixture is formed. Solutions are highly advantageous since each drop is an aliquot and in each aliquot, the distribution of anions and cations is uniform. In some cases some of the ingredients are not readily soluble and then the material can be milled in the solvent for a sufficient time to reduce it into colloidal-like state. It can then be readily admixed with the solution. Thus, in each droplet which will be formed, the composition is substantially identical. Moreover, each droplet will be substantially equal in size and thus when the solvent is evaporated, each resulting particle will also be substantially uniform in size.

The solution is sprayed through nozzles under requisite pressure into a heated stream of gas which will not deleteriously react with the solute at the temperature involved. The temperature is controlled so that it is sufficient to vaporize the solute, but insufficient to volatilize any significant quantities of the components of the phosphor. With some of the compositions, a single pass of the droplets through the heated gas will be sufficient for activation and formation of a phosphor. In other cases, the phosphor spheres will have to be fired sequentially to activate the material, as is conventional in the art.

When fabricating lamps, the spherical phosphor is then stirred with a volatile vehicle and a small amount of vehicle-soluble binder to form a phosphor-vehicle suspension or so-called paint which is suitable for coating a fluorescent lamp envelope. As a specific example, 400 grams of the phosphor

are mixed with 440 cc. of xylol and 110 cc. of butanol, together with 14 grams of ethyl cellulose having a viscosity of 300 cps. The mixture is stirred with any conventional power-driven stirring mechanism for a period of approximately ½ hour for example. This forms a homogeneous suspension or paint of the very finely divided phosphor material. This paint may be further thinned if desired. The prepared paint is flushed over the inside of a fluorescent tube, after which the ethyl cellulose binder is volatilized by lehring the coated tube at a temperature of about 650° C for about 3 minutes for example. Thereafter lamp fabrication is completed in accordance with conventional practice.

The paint vehicle and vehicle-soluble binder are also subject to considerable variation as are the relative proportions of phosphor and vehicle which comprise the paint. While ethyl cellulose binder and xylol-butanol vehicle have been given in the preferred example, a vehicle and vehicle-soluble binder of butyl acetate and nitrocellulose or water and methyl cellulose or other organic binder can be substituted for the xylol butanol vehicle and ethyl cellulose binder.

The following table illustrates the advantages of using spherical phosphors in lamps. Lamps using hollow spheroidal tin activated, calcium, magnesium strontium orthophosphate were compared to ones which were coated with particulate material of the same compositions. The coating on each was prepared so that an optimum optical density of 78.5 was attained. Optical density is a relative method of measuring the transmission of a beam of white light through a lamp envelope. The covering ability of the measured material can be determined by using this technique.

Phosphor Type	Average Particle Size	Optical Density	Powder Weight
particulate spheroidal	10 μ	78.4	7.3 gms
	10 μ	78.5	3.22 gms

As seen from the above table, more than twice the weight of the particulate phosphor is needed to achieve a substantially similar optical density to that which was achieved when spheroidal phosphors were used.

The following specific examples are given as further explanations and are not intended to be limitative upon the claims.

EXAMPLE I

A calcium halophosphate phosphor can be prepared by dissolving the following ingredients in 20,000 cc. of water acidified with 5,000 cc. of concentrated HNO₃.

Material	Gram Moles
CaHPO ₄	2.94
CdNH ₄ PO ₄	0.06
CaCO ₃	1.35
CaF ₂	0.40
NH ₄ Cl	0.30
MnCO ₃	0.08
Sb ₂ O ₃	0.06

The solution is sprayed into a stream of nitrogen which is heated to a temperature of about 500° C and the solvent is volatilized. The material is then fired in nitrogen at 1,260° C and a luminescent calcium fluorochlorophosphate activated by manganese and antimony is formed.

EXAMPLE II

A solution is made by dissolving the following in 20,000 cc. of water acidified with 5,000 cc. of concentrated HNO₃

Material	Moles
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Y ₂ O ₃	0.5
Eu ₂ O ₃	0.035
NH ₄ VO ₃	1.0

The ingredients are sprayed into a stream of nitrogen at about 550° C and the material is then fired at 950° C in an air atmosphere to activate the phosphor. A red emitting europium activated yttrium vanadate phosphor is formed. The phosphor has spherical shape.

EXAMPLE III

A solution is formed by dissolving the following ingredients in 20,000 cc. of water acidified with 5,000 cc. of HNO₃

Material	Moles
Sr(H ₂ PO ₄) ₂	1.985
Cu ₂ Cl ₂	0.005
(NH ₄) ₂ HPO ₄	0.01

The solution is sprayed into a stream of air at 500° C and the solvent is volatilized leaving porous, hollow spheres of material. The material is then fired in air at 1,600° F and red-emitting copper activated, strontium metaphosphate phosphor is formed.

EXAMPLE IV

A solution is formed by dissolving the following ingredients in 20,000 cc. of H₂O with 5,000 cc. of HNO₃

Material	Moles
MgO	0.992
SnO ₂	0.292
TiO ₂	0.187
H ₃ BO ₃	0.323

The solution is sprayed through a spray nozzle into a stream of air at 500° C and the solvent is volatilized leaving dried, hollow, porous spheres. The material is fired in an air atmosphere at 1,220° C and a bright blue emitting, spherical titanium and tin activated magnesium borate phosphor is produced.

EXAMPLE V

A solution of the following ingredients was formed and sprayed through a nozzle so as to form droplets.

Material	Moles
BaHPO ₄	11.99
Mg ₂ P ₂ O ₇	2.00
(NH ₄) ₄ HPO ₄	0.32
SnO	0.40
NH ₄ Cl	2.07

The droplets were passed through a stream of hot nitrogen gas at a temperature of about 500° C for a sufficient time to volatilize the solvent and leave porous, hollow spheres. The material was then fired in covered crucibles at 1,700° F and a blue green emitting α BaMgP₂O₇:Sn phosphor was produced.

EXAMPLE VI

A solution of the following ingredients was formed by dissolving them in 20,000 cc. of water mixed with 5,000 cc. of concentrated HNO₃. The Cd₂Sb₂O₇ is not readily soluble, so it is milled in some of the solvent for a sufficient time to make it colloidal and then this suspension is added to the rest of the solution.

Material	Moles
CaHPO ₄	3.00
CaCO ₃	0.01
CaF ₂	0.005
NH ₄ Cl	0.005
MnCO ₃	0.0007
Cd ₂ Sb ₂ O ₇	0.00005

The materials are sprayed into a hot stream of nitrogen at about 500° C and the solvent is volatilized leaving hollow, porous spheres. These spheres were fired in covered crucibles at 1,150° C. The spherical phosphor was a white emitting, calcium chlorofluorophosphate activated by antimony and manganese and containing cadmium in the matrix.

It is apparent that modifications and changes can be made within the spirit and scope of the present invention, but it is our intention only to be limited by the following claims.

- As our invention, we claim:
1. A fluorescent lamp comprising: a tubular glass envelope sealed at the ends; means to produce exciting radiation in said envelope; a phosphor coating disposed on the inner surface of said envelope and arranged so as to be irradiated by said exciting radiation; said phosphor coating comprised of at least one phosphor which has a substantial proportion of its particles in the form of spheroidal phosphor bodies.
 2. The lamp according to claim 1 wherein said spheroidal phosphor bodies have a diameter between about 3 and 20μ.
 3. The lamp according to claim 1 wherein a substantial proportion of said spheroidal phosphor bodies are hollow and have a wall thickness between about 0.5 and 8μ.

4. The lamp according to claim 3 wherein said spheroidal phosphor bodies have a diameter between about 3 and 20μ.
5. A high pressure electric discharge device comprising: a bulbous jacket with an arc tube disposed therein; means to produce exciting radiation within said arc tube; a phosphor coating disposed on the inner surface of said jacket and arranged so as to be irradiated by said exciting radiation, said phosphor coating comprised of at least one phosphor which has a substantial proportion of its particles in the form of spheroidal phosphor bodies.
6. The lamp according to claim 5 wherein said spheroidal phosphor bodies have a diameter between about 3 and 20μ.
7. The lamp according to claim 5 wherein a substantial proportion of said spheroidal bodies are hollow and have a wall thickness between about 0.5 and 8μ.
8. The lamp according to claim 7 wherein said spheroidal phosphor bodies have a diameter between about 3 and 20μ.
9. A cathode ray tube having, at one end, at least one electron gun from which electrons are beamed and, at the other end, a face panel; a coating of cathodoluminescent phosphor disposed upon said face panel and operatively associated with the beam from said gun; said phosphor coating having a substantial porportion of its particles in the form of spheroidal phosphor bodies.
10. The tube according to claim 9 wherein said spheroidal phosphor bodies have a diameter between about 3 and 20μ.
11. The tube according to claim 9 wherein a substantial proportion of said spheroidal bodies are hollow and have a wall thickness between about 0.5 and 8μ.
12. The tube according to claim 11 wherein said spheroidal phosphor bodies have a diameter between about 3 and 20μ.

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