

DUPLICATE

Our Ref.: OP-35

- 1 -

METHOD FOR RECLAIMING PIGMENT-ATTACHED RED-EMITTING
PHOSPHOR

The present invention relates to a method for
5 reclaiming a pigment-attached red-emitting phosphor
recovered from a manufacturing process for a color
picture tube, such as a red iron oxide-attached europium-
activated yttrium oxysulfide or a red iron oxide-attached
europium-activated yttrium oxide.

10 A fluorescent layer of a color picture tube is formed
in such a manner that each of green-, blue- and red-
emitting phosphors is mixed with predetermined
proportions of polyvinyl alcohol, ammonium dichromate, a
surfactant, etc. to obtain a phosphor slurry, which is
15 then coated over the entire surface of a face plate
having a black matrix preformed by carbon, by a suitable
coating method such as a spin coating method, then
ultraviolet rays are irradiated through a shadow mask or
an aperture grille to cure the predetermined portions,
20 followed by developing with warm water. This operation

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is repeated with respect to three color-emitting phosphors to form a fluorescent layer with a predetermined arrangement of dots or stripes.

Phosphor slurries dripped or shaken off from the face
5 plate in the above coating step and phosphors washed off by water in the developing step are recovered. Among such recovered phosphors, a red-emitting phosphor containing expensive rare earth elements, will certainly be reclaimed and reused.

10 The red-emitting phosphor slurry recovered in the coating step contains blue- and green-emitting phosphors as contaminants in addition to polyvinyl alcohol and ammonium dichromate as constituting components of the phosphor slurry. The red-emitting phosphor slurry
15 recovered in the developing step is the one which is obtained by washing non-exposed portions with developing water and thus contains substantial amounts of other color emitting phosphors.

Such recovered red-emitting phosphor will be purified
20 for reuse, by removing impurities. Among the impurities, organic substances may be removed by treatment with an oxidizing agent, alkali treatment or pyrolytic treatment (400 to 450°C), and a blue-emitting phosphor contaminant such as ZnS:Ag and a green-emitting phosphor contaminant
25 such as ZnS:Cu,Al may be removed by dissolving them with sodium hypochlorite or a mineral acid (such as HCl, H₂SO₄ and HNO₃).



However, when treated with a mineral acid, yttrium
oxysulfide as a host material of the red-emitting
phosphor will be partially dissolved to generate hydrogen
sulfide. This hydrogen sulfide will react with heavy
5 metal ions such as copper ions or silver ions which may
be present in the system, to form hardly soluble CuS,
AgS, etc., which will firmly adhere to the phosphor
surface. Such adherence impairs the phosphor surface
property and adversely affects the emitting property and
10 the coating property. Further, the dissolution of the
host material causes exfoliation of the pigment attached
to the phosphor. Accordingly, it is required to reattach
the pigment to the phosphor before reuse. This adds to
the manufacturing cost. The use of a strong acid
15 necessitates washing with water repeatedly and thus
requires a long time for treatment and extra cost for
equipment.

In the treatment with an alkali or with an oxidizing
agent, a strong alkali or a large amount of an oxidizing
20 agent is required, to completely remove blue- and green-
emitting phosphors. Besides, under such a treating
condition, the phosphor will be oxidized, whereby the
luminance will be reduced. Further, most of the pigment
will be exfoliated by the exfoliation of binder, and it
25 will be necessary to reattach pigment before reuse.

It is an object of the present invention to overcome
the above drawbacks and to provide a treating method for



reclaiming a pigment-attached red-emitting phosphor, whereby not only blue- and green-emitting phosphors can be completely removed while preventing the pigment from exfoliation by suppressing dissolution of the binder
5 which attaches the pigment to the phosphor, but also deterioration of the luminance and the coating property, can be prevented.

The present invention provides a method for reclaiming a pigment-attached red-emitting phosphor
10 recovered from a manufacturing process for a color picture tube, which comprises treating the phosphor with an aqueous solution containing NaOH, NaClO and H₂O₂ and subsequently treating it with a weak acid.

Now, the present invention will be described in
15 detail with reference to the preferred embodiments.

The red-emitting phosphor suitable for the treating method of the present invention is a Eu-activated Y₂O₂S phosphor or a Eu-activated Y₂O₃ phosphor, to which a red pigment such as red ion oxide is attached by means of a
20 synthetic rubber such as an acrylic resin and a SBR resin. Such a phosphor may be covered with silica. To prepare a color picture tube, a red-emitting phosphor is used together with a Ag,Cl-activated ZnS blue-emitting phosphor, a Cu,Al-activated ZnS green-emitting phosphor
25 and a Cu,Au,Al-activated ZnS green-emitting phosphor, or together with such blue- and green-emitting phosphors having pigments attached thereto. Accordingly, the



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recovered red-emitting phosphor slurry contains such blue- and green-emitting phosphors as contaminants.

The treating solution to be used in the method of the present invention, is adjusted preferably to contain NaOH
5 at a concentration of from 0.3 to 4.0% by weight, NaClO at a concentration of from 1.0 to 5.0% by weight and H_2O_2 at a concentration of from 0.5 to 3.0% by weight, based on the solid content of the phosphor slurry.

If the concentrations exceed these ranges, the
10 oxidizing effect of the treating solution will be so strong that the luminance and the coating property of the phosphor will be deteriorated. On the other hand, if the concentrations are below the ranges, it is likely that the blue- and green-emitting phosphors, polyvinyl
15 alcohol, etc. can not be removed to a practical level. The treatment is conducted preferably at a temperature of at least 70°C.

In the weak acid treatment, dilute sulfuric acid, dilute hydrochloric acid, acetic acid or the like may be
20 used. It is preferable that such a weak acid is added to the phosphor slurry so that the pH of the slurry is adjusted to from 2 to 3, and the slurry is stirred and then washed with water repeatedly until the pH becomes at least 4.

25 The present invention is directed to a method which comprises treating a red pigment-attached phosphor recovered from a manufacturing process for a color



picture tube, with an aqueous solution containing NaOH, NaClO and H₂O₂, and subsequently removing the oxide produced by such an oxidizing agent with a weak acid, and thus designed to completely remove blue- and green-emitting phosphors contained as contaminants in the recovered red-emitting phosphor slurry, while preventing the pigment from exfoliation by suppressing the dissolution of the binder which attaches the pigment to the phosphor. The method of the present invention is effective for preventing deterioration of the luminance and the coating property of the red-emitting phosphor.

The surface of the reclaimed phosphor is preferably treated with gelatin, gum arabic and coating agent ZnSO₄, to improve the property of the slurry of the reclaimed phosphor.

A fresh red-emitting phosphor is added to the reclaimed red-emitting phosphor usually in a proportion of the fresh phosphor/the reclaimed phosphor of from 20/80 to 50/50 for reuse.

Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted to such specific Examples.

Example for the preparation of pigment-attached red-emitting phosphor

600ℓ of pure water was added to a slurry containing 300 kg of a Eu-activated Y₂O₂S phosphor, and 480 g of red



iron oxide was added thereto with stirring. A solution having 180 g of gelatin and 180 g of gum arabic dissolved in warm water, and 120 g of a SBR resin (as solid content) were added thereto and stirred for 20 minutes.

- 5 After adjusting the pH to 4.2 by acetic acid and stirring for 30 minutes, 1.5% of a glutaraldehyde curing agent was added and the resulting slurry was stirred for 60 minutes and left to stand still overnight.

Then, coating agent ZnSO_4 was added thereto, the pH
10 of the slurry was adjusted and the slurry was stirred for 20 minutes.

The resulting slurry was dehydrated, dried and worked up by sieving to obtain a red iron oxide-attached Eu-activated $\text{Y}_2\text{O}_2\text{S}$ phosphor.

15 Example for the manufacture of cathode-ray tubes

To an aqueous solution of polyvinyl alcohol, the above red iron oxide-attached Eu-activated $\text{Y}_2\text{O}_2\text{S}$ phosphor, a dispersant, an anti-foaming agent, etc. were added in a conventional manner and thoroughly stirred,
20 and ammonium dichromate sensitizer was added thereto obtain a red-emitting phosphor slurry.

Separately, blue- and green-emitting phosphor slurries were prepared in the same manner as for the red-emitting phosphor slurry, by using a Ag,Cl-activated ZnS
25 phosphor as a blue-emitting phosphor and a Cu,Al-activated ZnS phosphor as a green-emitting phosphor. Then, a glass panel was coated with green-, blue- and



red-emitting phosphor slurries successively, followed by drying, exposure and development to obtain a color cathode-ray tube.

Example for reclaiming treatment of the recovered red-emitting phosphor

The red-emitting phosphor recovered in the developing step was subjected to reclaiming treatment under the following conditions.

Sample F:

- 10 300 kg, based on dry weight, of the recovered phosphor was added to 300ℓ of pure water, and the mixture was stirred for 30 minutes, followed by sieving to remove foreign substances. Subsequently, warm water was added to the resulting slurry to the total volume of 1,000ℓ.
- 15 After adjusting the temperature of the mixture to 75°C, the slurry was stirred for 20 minutes and left to stand still, and then, the supernatant was discarded. Warm water was added again to the obtained precipitate to the total volume of 700ℓ, and the temperature was adjusted to
- 20 75°C. While stirring, a treating solution comprising 1.5 kg of NaOH as an alkali, 60ℓ of 12.5% NaClO (based on effective chlorine) as an oxidizing agent and 8ℓ of 35% H₂O₂, was gradually added to the above slurry and the slurry mixture was stirred for 3 hours and left to stand
- 25 still to precipitate the phosphor, and the supernatant was discarded to remove polyvinyl alcohol, ammonium dichromate, etc. Warm water was further added to the



phosphor slurry to the total volume of 1,000ℓ. The resulting slurry was stirred for 20 minutes with the temperature adjusted to 75°C and left to stand still, and the supernatant was discarded.

5 To the above phosphor slurry, water was added to the total volume of 700ℓ, and 4N sulfuric acid was added to the phosphor slurry while stirring and maintaining the temperature at 25°C, to adjust the pH to 2.5. After stirring for 2.5 hours, the resulting slurry was left to
10 stand still, and the supernatant was discarded, followed by washing with water repeatedly so that the pH would be about 4.

To the phosphor slurry thus reclaimed, water was added to the total volume of 700ℓ, and the solution
15 having 180 g of gelatin and 180 g of gum arabic dissolved in warm water, was added thereto. After stirring for 20 minutes, the phosphor slurry was left to stand still, and the supernatant was discarded. After further adding water to the slurry to bring the total volume to 700ℓ,
20 coating agent ZnSO_4 was added, and the slurry was stirred for 20 minutes, dehydrated, dried and sieved, to treat the surface of the phosphor.

Sample A:

In the reclaiming treatment of Sample F, only the
25 initial washing treatment was conducted, and the treatment with the treating solution and subsequent treatments were omitted, to obtain a reclaimed phosphor,



which is designated as Sample A.

Sample B:

A slurry of a fresh red-emitting phosphor was prepared and used as a standard for the evaluation of
5 reclaimed phosphor slurries.

Sample C:

In the reclaiming treatment of Sample F, the recovered phosphor was treated in the same manner as for Sample F, except for omitting 3% NaClO from the treating
10 solution comprising 0.5% NaOH , 3% NaClO and 1.4% H_2O_2 , to obtain a reclaimed phosphor, which is designated as Sample C.

Sample D:

In the above reclaiming treatment of Sample C, the
15 recovered phosphor was treated in the same manner as for Sample C, except that the concentration of H_2O_2 of the treating solution was 14%, to obtain a reclaimed phosphor, which is designated as Sample D.

Sample E:

20 In the above reclaiming treatment of Sample F, the recovered phosphor was treated in the same manner as for Sample F, except that H_2O_2 was excluded from the treating solution comprising 0.5% NaOH , 3% NaClO and 1.4% H_2O_2 , to obtain a reclaimed phosphor, which is designated as
25 Sample E.

Evaluation of the reclaimed red-emitting phosphors

Phosphor slurries of Samples A to F, were evaluated



with respect to the items shown in Table 1. Sample F represents the phosphor reclaimed according to the method of the present invention.

① The luminance shown in Table 1 is a relative
5 luminance based on the luminance of the fresh standard phosphor being evaluated to be 100%.

② The powder reflectance of the phosphors was measured at a wavelength of 500 mm, considering that the powder reflectance is quite consistent with the hue (i.e.
10 the density) of red of the pigment-attached red-emitting phosphor.

③ The amount of the remaining ZnS was calculated from the Zn^{2+} content obtained by dissolving the reclaimed phosphor with a strong acid completely and
15 determining Zn^{2+} . This value corresponds to the total amount of the blue- and green-emitting phosphors remaining in the red-emitting phosphor. The larger the amount of the remaining ZnS, the smaller the value x in x/y, and this indicates that the peak of the fluorescence
20 emitted by the red-emitting phosphor was shifted to the short wavelength side.

④ The visually observed UV-stimulated color mixture was measured by coating the red-phosphor on a transparent glass plate by means of an alcohol and stimulating it by
25 ultraviolet light, whereupon the number of specks of blue- and green-emitting phosphors existing in a field of view of an optical microscope, was counted. It



corresponds to the amount of the remaining ZnS.

⑤ The amount of the remaining SBR binder was analyzed by pyrolysis gas chromatography, and calculated based on the value of the fresh red-emitting phosphor
5 being evaluated to be 100%. A decrease of the remaining SBR binder which attaches the pigment to the phosphor, indicates exfoliation of the pigment.



Table 1

Samples	Treating conditions	Characteristics of red-emitting phosphor		Powder reflectance (500 nm)	Amount of the remaining ZnS (%)	Visually observed UV-stimulated color mixture	Amount of the remaining SBR binder (%)
		x/y	Luminance (%)				
A	Recovered phosphor washed with water	0.657/0.332	101	58.6%	0.34	10	100
B	Fresh red-emitting phosphor slurry	0.663/0.334	100	52.0%	0.000	0	-
C	NaOH (0.5%) + H ₂ O ₂ (1.4%)	0.660/0.334	102	61.7%	0.04	10	79
D	NaOH (10%) + H ₂ O ₂ (14%)	0.663/0.334	83	62.0%	0.001	0	72
E	NaOH (0.5%) + NaClO (3%)	0.662/0.334	104	61.3%	0.003	0	81
F	NaOH (0.5%) + NaClO (3%) + H ₂ O ₂ (1.4%)	0.663/0.334	100	56.7%	0.000	0	100

Note: Sample F represents the phosphor reclaimed by the method of the present invention.



Among Samples C and D, which were treated with a treating solution comprising NaOH and H_2O_2 , Sample C had a large amount of remaining ZnS because of a lower concentration of H_2O_2 , and ten specks of ZnS, which is a host material of blue- and green-emitting phosphors, were observed by the visual observation of the UV-stimulated color mixture. Further, exfoliation of the pigment was confirmed by a decrease of the remaining SBR binder.

With respect to Sample D treated with an increased concentration of H_2O_2 , the decrease in the amount of the remaining SBR binder was substantial, and exfoliation of the pigment and the considerable reduction of luminance, were observed, although ZnS was sufficiently removed. The reduction of luminance seems to result from partial oxidization of the surface of the $Y_2O_2S:Eu$ phosphor by the oxidizing agent.

With respect to Sample E, which was treated with a treating solution comprising NaOH and $NaClO$, the removal of ZnS proceeded considerably as compared with Sample C, but the decrease in the amount of the remaining SBR binder was substantial, which indicates exfoliation of the pigment.

With respect to Sample F, an example treated by the method of the present invention, namely treated with a treating solution comprising NaOH, H_2O_2 and $NaClO$, ZnS was sufficiently removed, the amount of the remaining SBR binder was similar to that in Sample B of fresh phosphor,



no exfoliation of the pigment or no shift of the x/y value was observed, and the luminance was as high as that of Sample B.

According to the present invention, by adopting the
5 above construction, it is possible not only to prevent the pigment from exfoliation but also to completely remove blue- and green-emitting phosphors contained as contaminants in the recovered red-emitting phosphor, and the recovered red-emitting phosphor can be reclaimed
10 effectively to obtain a red-emitting phosphor with high luminance and a good coating property.

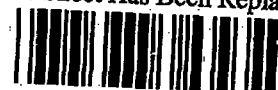




CLAIMS:

1. A method for reclaiming a pigment-attached red-emitting phosphor recovered from a manufacturing process for a color picture tube, which comprises treating the phosphor with an aqueous solution containing NaOH, NaClO and H₂O₂, and subsequently treating it with a weak acid.
2. The method according to Claim 1, wherein the pigment is attached to the red-emitting phosphor by a synthetic rubber such as an acrylic resin or a styrene-butadiene resin as a binder.
3. The method according to Claim 1, wherein the red-emitting phosphor is the one recovered from a manufacturing process for a color picture tube wherein a red iron oxide-attached europium-attached yttrium oxysulfide red-emitting phosphor or a red iron oxide-attached europium-activated yttrium oxide red-emitting phosphor, and blue- and green-emitting phosphors of which host materials are ZnS, are used.
4. The method according to Claim 1, wherein the aqueous solution contains NaOH at a concentration of from 0.3 to 4.0% by weight, NaClO at a concentration of from 1.0 to 5.0% by weight and H₂O₂ at a concentration of from 0.5 to 3.0% by weight, based on the solid content of the phosphor slurry to be treated.
5. The method according to Claim 1, wherein the weak acid is dilute sulfuric acid, dilute hydrochloric acid or acetic acid.

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- 17 -

6. The method according to Claim 1, wherein the treatment with the weak acid is conducted at a pH of from 2 to 3, followed by washing with water to a pH of at least 4.

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METHOD FOR RECLAIMING PIGMENT-ATTACHED RED-EMITTING PHOS
ABSTRACT

A method for reclaiming a pigment-attached red-emitting phosphor recovered from a manufacturing process for a color picture tube, which comprises treating the phosphor with an aqueous solution containing NaOH, NaClO and H₂O₂ and then treating it with a weak acid, whereby the pigment can be prevented from exfoliation by suppressing the dissolution of the binder which attaches the pigment to the phosphor, and blue- and green-emitting phosphors contained as contaminants in the recovered red-emitting phosphor can be completely removed. The method provides a reclaimed red-emitted phosphor with high luminance and a good coating property.



24 JUL 1996

- 1 -

METHOD FOR RECLAIMING PIGMENT-ATTACHED RED-EMITTING
PHOSPHOR

The present invention relates to a method for
5 reclaiming a pigment-attached red-emitting phosphor
recovered from a manufacturing process for a color
picture tube, such as a red iron oxide-attached europium-
activated yttrium oxysulfide or a red iron oxide-attached
europium-activated yttrium oxide.

10 A fluorescent layer of a color picture tube is formed
in such a manner that each of green-, blue- and red-
emitting phosphors is mixed with predetermined
proportions of polyvinyl alcohol, ammonium dichromate, a
surfactant, etc. to obtain a phosphor slurry, which is
15 then coated over the entire surface of a face plate
having a black matrix preformed by carbon, by a suitable
coating method such as a spin coating method, then
ultraviolet rays are irradiated through a shadow mask or
an aperture grille to cure the predetermined portions,
20 followed by developing with warm water. This operation

24 JUL 1996
emitting

is repeated with respect to three color-emitting phosphors to form a fluorescent layer with a predetermined arrangement of dots or stripes.

Phosphor slurries dripped or shaken off from the face plate in the above coating step and phosphors washed off by water in the developing step are recovered. Among such recovered phosphors, a red-emitting phosphor containing expensive rare earth elements, will certainly be reclaimed and reused.

10 The red-emitting phosphor slurry recovered in the coating step contains blue- and green-emitting phosphors as contaminants in addition to polyvinyl alcohol and ammonium dichromate as constituting components of the phosphor slurry. The red-emitting phosphor slurry
15 recovered in the developing step is the one which is obtained by washing non-exposed portions with developing water and thus contains substantial amounts of other color emitting phosphors.

Such recovered red-emitting phosphor will be purified
20 for reuse, by removing impurities. Among the impurities, organic substances may be removed by treatment with an oxidizing agent, alkali treatment or pyrolytic treatment (400 to 450°C), and a blue-emitting phosphor contaminant such as ZnS:Ag and a green-emitting phosphor contaminant
25 such as ZnS:Cu,Al may be removed by dissolving them with sodium hypochlorite or a mineral acid (such as HCl, H₂SO₄ and HNO₃).

24 JUL 1996

However, when treated with a mineral acid, yttrium oxysulfide as a host material of the red-emitting phosphor will be partially dissolved to generate hydrogen sulfide. This hydrogen sulfide will react with heavy metal ions such as copper ions or silver ions which may be present in the system, to form hardly soluble CuS, AgS, etc., which will firmly adhere to the phosphor surface. Such adherence impairs the phosphor surface property and adversely affects the emitting property and the coating property. Further, the dissolution of the host material causes exfoliation of the pigment attached to the phosphor. Accordingly, it is required to reattach the pigment to the phosphor before reuse. This adds to the manufacturing cost. The use of a strong acid necessitates washing with water repeatedly and thus requires a long time for treatment and extra cost for equipment.

In the treatment with an alkali or with an oxidizing agent, a strong alkali or a large amount of an oxidizing agent is required, to completely remove blue- and green-emitting phosphors. Besides, under such a treating condition, the phosphor will be oxidized, whereby the luminance will be reduced. Further, most of the pigment will be exfoliated by the exfoliation of binder, and it will be necessary to reattach pigment before reuse.

It is an object of the present invention to overcome the above drawbacks and to provide a treating method for



24 JUL 1996

reclaiming a pigment-attached red-emitting phosphor,
whereby not only blue- and green-emitting phosphors can

be completely removed while preventing the pigment from
exfoliation by suppressing dissolution of the binder

5 which attaches the pigment to the phosphor, but also
deterioration of the luminance and the coating property,
can be prevented.

The present invention provides a method for
reclaiming a pigment-attached red-emitting phosphor
10 recovered from a manufacturing process for a color
picture tube, which comprises treating the phosphor with
an aqueous solution containing NaOH, NaClO and H₂O₂ and
subsequently treating it with a weak acid.

Now, the present invention will be described in
15 detail with reference to the preferred embodiments.

The red-emitting phosphor suitable for the treating
method of the present invention is a Eu-activated Y₂O₂S
phosphor or a Eu-activated Y₂O₃ phosphor, to which a red
pigment such as red ion oxide is attached by means of a
20 synthetic rubber such as an acrylic resin and a SBR
resin. Such a phosphor may be covered with silica. To
prepare a color picture tube, a red-emitting phosphor is
used together with a Ag,Cl-activated ZnS blue-emitting
phosphor, a Cu,Al-activated ZnS green-emitting phosphor
25 and a Cu,Au,Al-activated ZnS green-emitting phosphor, or
together with such blue- and green-emitting phosphors
having pigments attached thereto. Accordingly, the



REPLACEMENT SHEET

24 JUL 1996

recovered red-emitting phosphor slurry contains such
blue- and green-emitting phosphors as contaminants.

The treating solution to be used in the method of the
present invention, is adjusted preferably to contain NaOH
5 at a concentration of from 0.3 to 4.0% by weight, NaClO
at a concentration of from 1.0 to 5.0% by weight and H₂O₂
at a concentration of from 0.5 to 3.0% by weight, based
on the solid content of the phosphor slurry.

If the concentrations exceed these ranges, the
10 oxidizing effect of the treating solution will be so
strong that the luminance and the coating property of the
phosphor will be deteriorated. On the other hand, if the
concentrations are below the ranges, it is likely that
the blue- and green-emitting phosphors, polyvinyl
15 alcohol, etc. can not be removed to a practical level.
The treatment is conducted preferably at a temperature of
at least 70°C.

In the weak acid treatment, dilute sulfuric acid,
dilute hydrochloric acid, acetic acid or the like may be
20 used. It is preferable that such a weak acid is added to
the phosphor slurry so that the pH of the slurry is
adjusted to from 2 to 3, and the slurry is stirred and
then washed with water repeatedly until the pH becomes at
least 4.

25 The present invention is directed to a method which
comprises treating a red pigment-attached phosphor
recovered from a manufacturing process for a color



24 JUL 1996

picture tube, with an aqueous solution containing NaOH, NaClO and H₂O₂, and subsequently removing the oxide produced by such an oxidizing agent with a weak acid, and thus designed to completely remove blue- and green-emitting phosphors contained as contaminants in the recovered red-emitting phosphor slurry, while preventing the pigment from exfoliation by suppressing the dissolution of the binder which attaches the pigment to the phosphor. The method of the present invention is effective for preventing deterioration of the luminance and the coating property of the red-emitting phosphor.

The surface of the reclaimed phosphor is preferably treated with gelatin, gum arabic and coating agent ZnSO₄, to improve the property of the slurry of the reclaimed phosphor.

A fresh red-emitting phosphor is added to the reclaimed red-emitting phosphor usually in a proportion of the fresh phosphor/the reclaimed phosphor of from 20/80 to 50/50 for reuse.

Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted to such specific Examples.

Example for the preparation of pigment-attached red-emitting phosphor

600g of pure water was added to a slurry containing 300 kg of a Eu-activated Y₂O₂S phosphor, and 480 g of red



24 JUL 1996

A solution

iron oxide was added thereto with stirring. having 180 g of gelatin and 180 g of gum arabic dissolved in warm water, and 120 g of a SBR resin (as solid content) were added thereto and stirred for 20 minutes.

- 5 After adjusting the pH to 4.2 by acetic acid and stirring for 30 minutes, 1.5% of a glutaraldehyde curing agent was added and the resulting slurry was stirred for 60 minutes and left to stand still overnight.

- 10 Then, coating agent ZnSO_4 was added thereto, the pH of the slurry was adjusted and the slurry was stirred for 20 minutes.

The resulting slurry was dehydrated, dried and worked up by sieving to obtain a red iron oxide-attached Eu-activated $\text{Y}_2\text{O}_2\text{S}$ phosphor.

15 Example for the manufacture of cathode-ray tubes

- To an aqueous solution of polyvinyl alcohol, the above red iron oxide-attached Eu-activated $\text{Y}_2\text{O}_2\text{S}$ phosphor, a dispersant, an anti-foaming agent, etc. were added in a conventional manner and thoroughly stirred, and ammonium dichromate sensitizer was added thereto to obtain a red-emitting phosphor slurry.

- 25 Separately, blue- and green-emitting phosphor slurries were prepared in the same manner as for the red-emitting phosphor slurry, by using a Ag,Cl-activated ZnS phosphor as a blue-emitting phosphor and a Cu,Al-activated ZnS phosphor as a green-emitting phosphor.

Then, a glass panel was coated with green-, blue- and

24 JUL 1996

followed by

red-emitting phosphor slurries successively, followed by drying, exposure and development to obtain a color cathode-ray tube.

Example for reclaiming treatment of the recovered red-emitting phosphor

The red-emitting phosphor recovered in the developing step was subjected to reclaiming treatment under the following conditions.

Sample F:

- 300 kg, based on dry weight, of the recovered phosphor was added to 300ℓ of pure water, and the mixture was stirred for 30 minutes, followed by sieving to remove foreign substances. Subsequently, warm water was added to the resulting slurry to the total volume of 1,000ℓ.
- After adjusting the temperature of the mixture to 75°C, the slurry was stirred for 20 minutes and left to stand still, and then, the supernatant was discarded. Warm water was added again to the obtained precipitate to the total volume of 700ℓ, and the temperature was adjusted to 75°C. While stirring, a treating solution comprising 1.5 kg of NaOH as an alkali, 60ℓ of 12.5% NaClO (based on effective chlorine) as an oxidizing agent and 8ℓ of 35% H₂O₂, was gradually added to the above slurry and the slurry mixture was stirred for 3 hours and left to stand still to precipitate the phosphor, and the supernatant was discarded to remove polyvinyl alcohol, ammonium dichromate, etc. Warm water was further added to the



24 JUL 1996

phosphor slurry to the total volume of 1,000ℓ. The resulting slurry was stirred for 20 minutes with the temperature adjusted to 75°C and left to stand still, and the supernatant was discarded.

5 To the above phosphor slurry, water was added to the total volume of 700ℓ, and 4N sulfuric acid was added to the phosphor slurry while stirring and maintaining the temperature at 25°C, to adjust the pH to 2.5. After stirring for 2.5 hours, the resulting slurry was left to
10 stand still, and the supernatant was discarded, followed by washing with water repeatedly so that the pH would be about 4.

To the phosphor slurry thus reclaimed, water was added to the total volume of 700ℓ, and the solution
15 having 180 g of gelatin and 180 g of gum arabic dissolved in warm water, was added thereto. After stirring for 20 minutes, the phosphor slurry was left to stand still, and the supernatant was discarded. After further adding water to the slurry to bring the total volume to 700ℓ,
20 coating agent ZnSO_4 was added, and the slurry was stirred for 20 minutes, dehydrated, dried and sieved, to treat the surface of the phosphor.

Sample A:

In the reclaiming treatment of Sample F, only the
25 initial washing treatment was conducted, and the treatment with the treating solution and subsequent treatments were omitted, to obtain a reclaimed phosphor,

24 JUL 1996

which is designated as Sample A.

Sample B:

A slurry of a fresh red-emitting phosphor was prepared and used as a standard for the evaluation of
5 reclaimed phosphor slurries.

Sample C:

In the reclaiming treatment of Sample F, the recovered phosphor was treated in the same manner as for Sample F, except for omitting 3% NaClO from the treating
10 solution comprising 0.5% NaOH, 3% NaClO and 1.4% H₂O₂, to obtain a reclaimed phosphor, which is designated as Sample C.

Sample D:

In the above reclaiming treatment of Sample C, the
15 recovered phosphor was treated in the same manner as for Sample C, except that the concentration of H₂O₂ of the treating solution was 14%, to obtain a reclaimed phosphor, which is designated as Sample D.

Sample E:

20 In the above reclaiming treatment of Sample F, the recovered phosphor was treated in the same manner as for Sample F, except that H₂O₂ was excluded from the treating solution comprising 0.5% NaOH, 3% NaClO and 1.4% H₂O₂, to obtain a reclaimed phosphor, which is designated as
25 Sample E.

Evaluation of the reclaimed red-emitting phosphors

Phosphor slurries of Samples A to F, were evaluated

24 JUL 1996

with respect to the items shown in Table 1. Sample F represents the phosphor reclaimed according to the method of the present invention.

① The luminance shown in Table 1 is a relative
5 luminance based on the luminance of the fresh standard phosphor being evaluated to be 100%.

② The powder reflectance of the phosphors was measured at a wavelength of 500 nm, considering that the powder reflectance is quite consistent with the hue (i.e.
10 the density) of red of the pigment-attached red-emitting phosphor.

③ The amount of the remaining ZnS was calculated from the Zn^{2+} content obtained by dissolving the reclaimed phosphor with a strong acid completely and
15 determining Zn^{2+} . This value corresponds to the total amount of the blue- and green-emitting phosphors remaining in the red-emitting phosphor. The larger the amount of the remaining ZnS, the smaller the value x in x/y , and this indicates that the peak of the fluorescence
20 emitted by the red-emitting phosphor was shifted to the short wavelength side.

④ The visually observed UV-stimulated color mixture was measured by coating the red-phosphor on a transparent glass plate by means of an alcohol and stimulating it by
25 ultraviolet light, whereupon the number of specks of blue- and green-emitting phosphors existing in a field of view of an optical microscope, was counted. It

24 JUL 1996

corresponds to the amount of the remaining ins

- ⑤ The amount of the remaining SBR binder was analyzed by pyrolysis gas chromatography, and calculated based on the value of the fresh red-emitting phosphor being evaluated to be 100%. A decrease of the remaining SBR binder which attaches the pigment to the phosphor, indicates exfoliation of the pigment.

REPLACEMENT SHEET

24 JUL 1996

Table 1

Samples	Treating conditions	Characteristics of red-emitting phosphor		Powder reflectance (500 nm)	Amount of the remaining ZnS (%)	Visually observed UV-stimulated color mixture	Amount of the remaining SBR binder (%)
		x/y	Luminance (%)				
A	Recovered phosphor washed with water	0.657/0.332	101	58.6%	0.34	10	100
B	Fresh red-emitting phosphor slurry	0.663/0.334	100	52.0%	0.000	0	-
C	NaOH (0.5%) + H ₂ O ₂ (1.4%)	0.660/0.334	102	61.7%	0.04	10	79
D	NaOH (10%) + H ₂ O ₂ (14%)	0.663/0.334	83	62.0%	0.001	0	72
E	NaOH (0.5%) + NaClO (3%)	0.662/0.334	104	61.3%	0.003	0	81
F	NaOH (0.5%) + NaClO (3%) + H ₂ O ₂ (1.4%)	0.663/0.334	100	56.7%	0.000	0	100

Note: Sample F represents the phosphor reclaimed by the method of the present invention.

This Sheet Has Been Replaced



REPLACEMENT SHEET

24 JUL 1996

Among Samples C and D, which were treated with a treating solution comprising NaOH and H_2O_2 , Sample C had

a large amount of remaining ZnS because of a lower concentration of H_2O_2 , and ten specks of ZnS, which is a host material of blue- and green-emitting phosphors, were observed by the visual observation of the UV-stimulated color mixture. Further, exfoliation of the pigment was confirmed by a decrease of the remaining SBR binder.

With respect to Sample D treated with an increased concentration of H_2O_2 , the decrease in the amount of the remaining SBR binder was substantial, and exfoliation of the pigment and the considerable reduction of luminance, were observed, although ZnS was sufficiently removed. The reduction of luminance seems to result from partial oxidization of the surface of the $Y_2O_2S:Eu$ phosphor by the oxidizing agent.

With respect to Sample E, which was treated with a treating solution comprising NaOH and $NaClO$, the removal of ZnS proceeded considerably as compared with Sample C, but the decrease in the amount of the remaining SBR binder was substantial, which indicates exfoliation of the pigment.

With respect to Sample F, an example treated by the method of the present invention, namely treated with a treating solution comprising NaOH, H_2O_2 and $NaClO$, ZnS was sufficiently removed, the amount of the remaining SBR binder was similar to that in Sample B of fresh phosphor,

REPLACEMENT SHEET

24 JUL 1996

no exfoliation of the pigment or no shift of the x/y value was observed, and the luminance was as high as that of Sample B.

According to the present invention, by adopting the
5 above construction, it is possible not only to prevent the pigment from exfoliation but also to completely remove blue- and green-emitting phosphors contained as contaminants in the recovered red-emitting phosphor, and the recovered red-emitting phosphor can be reclaimed
10 effectively to obtain a red-emitting phosphor with high luminance and a good coating property.



- 16 -

REPLACEMENT SHEET

24 JUL 1996

CLAIMS:

1. A method for reclaiming a pigment-attached ~~red~~ emitting phosphor recovered from a manufacturing process for a color picture tube, which comprises treating the phosphor with an aqueous solution containing NaOH, NaClO and H₂O₂, and subsequently treating it with a weak acid.
2. The method according to Claim 1, wherein the pigment is attached to the red-emitting phosphor by a synthetic rubber such as an acrylic resin or a styrene-butadiene resin as a binder.
3. The method according to Claim 1, wherein the red-emitting phosphor is the one recovered from a manufacturing process for a color picture tube wherein a red iron oxide-attached europium-attached yttrium oxysulfide red-emitting phosphor or a red iron oxide-attached europium-activated yttrium oxide red-emitting phosphor, and blue- and green-emitting phosphors of which host materials are ZnS, are used.
4. The method according to Claim 1, wherein the aqueous solution contains NaOH at a concentration of from 0.3 to 4.0% by weight, NaClO at a concentration of from 1.0 to 5.0% by weight and H₂O₂ at a concentration of from 0.5 to 3.0% by weight, based on the solid content of the phosphor slurry to be treated.
5. The method according to Claim 1, wherein the weak acid is dilute sulfuric acid, dilute hydrochloric acid or acetic acid.

This Sheet Has Been Replaced



REPLACEMENT SHEET

24 JUL 1996

6. The method according to Claim 1, wherein the treatment with the weak acid is conducted at a pH of from 2 to 3, followed by washing with water to a pH of at least 4.



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REPLACEMENT SHEET

24 JUL 1996

METHOD FOR RECLAIMING PIGMENT - ATTACHED
RED-EMITTING PHOSPHOR

ABSTRACT

A method for reclaiming a pigment-attached red-emitting phosphor recovered from a manufacturing process for a color picture tube, which comprises treating the phosphor with an aqueous solution containing NaOH, NaClO
5 and H₂O₂ and then treating it with a weak acid, whereby the pigment can be prevented from exfoliation by suppressing the dissolution of the binder which attaches the pigment to the phosphor, and blue- and green-emitting
10 phosphors contained as contaminants in the recovered red-emitting phosphor can be completely removed. The method provides a reclaimed red-emitted phosphor with high luminance and a good coating property.

REPLACEMENT SHEET
03 MAY 1997

However, when treated with a mineral acid, yttrium
oxysulfide as a host material of the red-emitting
phosphor will be partially dissolved to generate hydrogen
sulfide. This hydrogen sulfide will react with heavy
5 metal ions such as copper ions or silver ions which may
be present in the system, to form hardly soluble CuS,
AgS, etc., which will firmly adhere to the phosphor
surface. Such adherence impairs the phosphor surface
property and adversely affects the emitting property and
10 the coating property. Further, the dissolution of the
host material causes exfoliation of the pigment attached
to the phosphor. Accordingly, it is required to reattach
the pigment to the phosphor before reuse. This adds to
the manufacturing cost. The use of a strongly acidic pH
15 necessitates washing with water repeatedly and thus
requires a long time for treatment and extra cost for
equipment.

In the treatment with an alkali or with an oxidizing
agent, a strong alkaline pH or a large amount of an oxidizing
20 agent is required, to completely remove blue- and green-
emitting phosphors. Besides, under such a treating
condition, the phosphor will be oxidized, whereby the
luminance will be reduced. Further, most of the pigment
will be exfoliated by the exfoliation of binder, and it
25 will be necessary to reattach pigment before reuse.

It is an object of the present invention to overcome
the above drawbacks and to provide a treating method for

03 MAY 1997

reclaiming a pigment-attached red-emitting phosphor,
whereby not only blue- and green-emitting phosphors can
be completely removed while preventing the pigment from
exfoliation by suppressing dissolution of the binder
5 which attaches the pigment to the phosphor, but also
deterioration of the luminance and the coating property,
can be prevented.

The present invention provides a method for
reclaiming a pigment-attached red-emitting phosphor
10 recovered from a manufacturing process for a color
picture tube, which comprises treating the phosphor with
an aqueous solution containing NaOH, NaClO and H₂O₂ and
subsequently treating it with an acid.

Now, the present invention will be described in
15 detail with reference to the preferred embodiments.

The red-emitting phosphor suitable for the treating
method of the present invention is a Eu-activated Y₂O₂S
phosphor or a Eu-activated Y₂O₃ phosphor, to which a red
pigment such as red ion oxide is attached by means of a
20 synthetic rubber such as an acrylic resin and a SBR
resin. Such a phosphor may be covered with silica. To
prepare a color picture tube, a red-emitting phosphor is
used together with a Ag,Cl-activated ZnS blue-emitting
phosphor, a Cu,Al-activated ZnS green-emitting phosphor
25 and a Cu,Au,Al-activated ZnS green-emitting phosphor, or
together with such blue- and green-emitting phosphors
having pigments attached thereto. Accordingly, the

03 MAY 1997

recovered red-emitting phosphor slurry contains such
blue- and green-emitting phosphors as contaminants.

The treating solution to be used in the method of the
present invention, is adjusted preferably to contain NaOH
5 at a concentration of from 0.3 to 4.0% by weight, NaClO
at a concentration of from 1.0 to 5.0% by weight and H₂O₂
at a concentration of from 0.5 to 3.0% by weight, based
on the solid content of the phosphor slurry.

If the concentrations exceed these ranges, the
10 oxidizing effect of the treating solution will be so
strong that the luminance and the coating property of the
phosphor will be deteriorated. On the other hand, if the
concentrations are below the ranges, it is likely that
the blue- and green-emitting phosphors, polyvinyl
15 alcohol, etc. can not be removed to a practical level.
The treatment is conducted preferably at a temperature of
at least 70°C.

In the acid treatment, dilute sulfuric acid,
dilute hydrochloric acid, acetic acid or the like may be
20 used. It is preferable that such an acid is added to
the phosphor slurry so that the pH of the slurry is
adjusted to from 2 to 3, and the slurry is stirred and
then washed with water repeatedly until the pH becomes at
least 4.

25 The present invention is directed to a method which
comprises treating a red pigment-attached phosphor
recovered from a manufacturing process for a color

03 MAY 1997

picture tube, with an aqueous solution containing NaClO and H_2O_2 , and subsequently removing the oxide produced by such an oxidizing agent with an acid, and thus designed to completely remove blue- and green-emitting phosphors contained as contaminants in the recovered red-emitting phosphor slurry, while preventing the pigment from exfoliation by suppressing the dissolution of the binder which attaches the pigment to the phosphor. The method of the present invention is effective for preventing deterioration of the luminance and the coating property of the red-emitting phosphor.

The surface of the reclaimed phosphor is preferably treated with gelatin, gum arabic and coating agent ZnSO_4 , to improve the property of the slurry of the reclaimed phosphor.

A fresh red-emitting phosphor is added to the reclaimed red-emitting phosphor usually in a proportion of the fresh phosphor/the reclaimed phosphor of from 20/80 to 50/50 for reuse.

Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted to such specific Examples.

Example for the preparation of pigment-attached red-emitting phosphor

600g of pure water was added to a slurry containing 300 kg of a Eu-activated $\text{Y}_2\text{O}_2\text{S}$ phosphor, and 480 g of red

03 MAY 1997

red-emitting phosphor slurries successively, followed by drying, exposure and development to obtain a color cathode ray tube.

5

Example for reclaiming treatment of the recovered red-emitting phosphor

10 The red-emitting phosphor recovered in the developing step was subjected to reclaiming treatment under the following conditions.

Sample F:

15 300 kg, based on dry weight, of the recovered phosphor was added to 300 litres of pure water, and the mixture was stirred for 30 minutes, followed by sieving to remove foreign substances. Subsequently, warm water was added to the resulting slurry to the total volume of 1,000 litres.

20 After adjusting the temperature of the mixture to 75°C, the slurry was stirred for 20 minutes and left to stand still, and then, the supernatant was discarded. Warm water was added again to the obtained precipitate to the total volume of 700 litres, and the temperature was adjusted to 75°C.

25 While stirring, 1.5 kg of NaOH as an alkali, 60 litres of 12.5% NaClO (based on effective chlorine) as an oxidizing agent and 8 litres of 35% H₂O₂, were gradually added in this order to the above slurry, so as to make a NaOH content of 0.5%, a NaClO content of 2.5%, and a H₂O₂ content of 0.9% on

30 the basis of the solid content of the phosphor slurry, and the slurry mixture was stirred for 3 hours and left to stand still to precipitate the phosphor, and the supernatant was discarded to remove polyvinyl alcohol, ammonium dichromate, etc. Warm water was further added to the

35

03 MAY 1997

Table 1.

Samples	Treating conditions	Characteristics of red-emitting phosphor		Powder reflectance (500 nm)	Amount of the remaining ZnS (%)	Visually observed UV-stimulated color mixture	Amount of the remaining SDR binder (%)
		x/y	Luminance (%)				
A	Recovered phosphor washed with water	0.657/0.332	101	58.6%	0.34	10	100
B	Fresh red-emitting phosphor slurry	0.663/0.334	100	52.0%	0.000	0	100
C	NaOH (0.5%) + H ₂ O ₂ (1.4%)	0.660/0.334	102	61.7%	0.04	10	79
D	NaOH (10%) + H ₂ O ₂ (1.4%)	0.663/0.334	83	62.0%	0.001	0	72
E	NaOH (0.5%) + NaClO (3%)	0.662/0.334	104	61.3%	0.003	0	81
F	NaOH (0.5%) + NaClO (3%) + H ₂ O ₂ (1.4%)	0.663/0.334	100	56.7%	0.000	0	100

Note: Sample F represents the phosphor reclaimed by the method of the present invention.

03 MAY 1997

CLAIMS:



- 5 1. A method for reclaiming a pigment-attached red-emitting phosphor recovered from a manufacturing process for a color picture tube, which comprises treating the phosphor with an aqueous solution containing NaOH, NaClO and H₂O₂, and subsequently treating it with an acid.
- 10
2. The method according to Claim 1, wherein the pigment is attached to the red-emitting phosphor by a synthetic rubber as a binder.
- 15
3. The method according to Claim 1, wherein said color picture tube contains a red iron oxide-attached europium-activated yttrium oxysulfide red-emitting phosphor or a red
- 20 iron oxide-attached europium-activated yttrium oxide red-emitting phosphor, an Ag,Cl-activated ZnS blue-emitting phosphor having a pigment attached thereto, and a Cu,Al- or Cu,Au,Al-activated ZnS green-emitting phosphor.
- 25
4. The method according to Claim 1, wherein the aqueous solution contains NaOH at a concentration of from 0.3 to 4.0% by weight, NaClO at a concentration of from 1.0 to 5.0% by weight and H₂O₂ at a concentration of from 0.5 to 3.0% by
- 30 weight, based on the solid content of the phosphor slurry to be treated.
5. The method according to Claim 1, wherein the acid is
- 35 dilute sulfuric acid, dilute hydrochloride acid or acetic acid.



REPLACEMENT SHEET

03 MAY 1991

6. The method according to claim 1, wherein the treatment
with the acid is conducted at a pH of from 2 to 3, followed
5 by washing with water to a pH of at least 4.

7. The method according to Claim 2, wherein said synthetic
rubber is an acrylic resin or a styrene-butadiene rubber.