

PATENT SPECIFICATION

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(54) RED-PHOSPHOR RECOVERY

(71) We, INTERNATIONAL STANDARD ELECTRIC CORPORATION, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of 320 Park Avenue, New York 22, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method and an apparatus for separating a red rare-earth phosphor from a sediment.

The viewing screen of a colour-picture tube is comprised of a plurality of regularly arranged groups of three round or line-like phosphor dots which, depending on the type of phosphor used, emit green, blue or red light, respectively, when bombarded by electrons. Each colour is excited by one out of three electron guns contained in the picture tube.

In the most widely used method of making such colour picture screens, the phosphors are applied to the screen photochemically. An aqueous suspension or dispersion containing the phosphor to be applied and, as a photosensitive material, polyvinyl alcohol with ammonium bichromate, for example, is applied to the screen. A thin coating settles down, excess dispersion being removed by decanting and collected. From this dispersion, the phosphor is recovered by means of a centrifuge. The applied coating is dried and then exposed to light through a shadow mask having circular holes or an "aperture grille". In the exposed places, the polyvinyl alcohol becomes insoluble in water and binds the embedded phosphor at the surface of the screen. In the unexposed places, the coating is removed by rinsing, and the rinsing water with suspension dissolved therein is collected. This is done

for each of the three colours. The phosphors are usually applied in the order green - blue - red, mostly using copper-activated zinc-cadmium sulfide for green, silver-activated zinc sulfide for blue, and a europium- or samarium-activated rare-earth oxysulfide, such as europium-activated yttrium oxysulfide, for red. In former years, use was also made of zinc selenides and zinc-cadmium selenides and of rare-earth oxides and vanadates.

Only a small portion of a phosphor is deposited on the screen by the exposure to light, while the greater portion is subsequently rinsed out again, so considerable amounts of phosphor are left as residues. As the ratio of the prices per kilogramme of the phosphors green, blue and red is approximately 1:0.5:10, there is a special interest in recovering at least the red phosphor. Since the red phosphor is deposited last, the rinsed-out red phosphor from the unexposed portion of the screen unavoidably includes portions of the previously deposited phosphors. To recover this red phosphor, a number of methods are known, such as those disclosed in U.S. Patent 3,474,040 and German Published Patent Application (DT-OS) 2,126,893.

Both in the centrifuge and with any of the above-mentioned methods of recovery, a certain percentage is lost by being carried off in the sewers. To this must be added the phosphor which is washed out from scrap faceplates and scrap envelopes. At the current production rates of colour-picture tubes, therefore, so much sediment including red phosphor accumulates in the drain channels of a screen-coating room that, in view of the high price per kilogramme of the red phosphor, recovery from this sediment would be of great advantage.

According to the present invention there is provided a method of separating a red

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rare-earth phosphor from the sediment in the drain channels of a cathode ray tube screen-coating room, which sediment contains, in addition to various impurities, zinc - sulfide - base and zinc - cadmium - sulfide - base green and blue phosphors, including processing the sediment in the following sequential steps:

5 a. removing coarse foreign matter by sieving;

10 b. washing out constituents soluble in water, such as polyvinyl alcohol, ammonium bichromate, etc.;

15 c. heating to approximately 450°C, to volatilize further organic constituents;

20 d. cooling and pulverizing;

25 e. forming into an aqueous ammonium-halide dispersion;

30 f. electrolysis during passage between graphite electrodes;

35 g. filtering off sulphur and cathode deposit;

40 h. collecting in a tank, allowing solid constituents to deposit, and decanting the liquid;

45 i. preferably repeating the steps c to h, and

50 j. carrying out one of the known methods of regenerating only slightly contaminated rare-earth phosphors.

55 One such known regenerating method is that disclosed in DT-OS 2,126,893. The red rare-earth phosphor, unmixed or mixed with phosphor straight from the factory, is to be suitable for use in the manufacture of screens.

60 The invention will now be described in detail with reference to the accompanying drawing. The single figure of the drawing shows schematically one stage of the flow-electrolysis apparatus used in the method according to the invention. The washing, filtering, drying, and pulverizing equipment is of conventional design and its construction and operation is generally known, so it need not be shown and described here in detail.

65 To remove any coarse foreign matter, the sediment from the drain channels of a screen-coating room is first passed through a sieve whose apertures are approximately 100 μm in diameter. Residues of ammonium bichromate, polyvinyl alcohol and other substances soluble in water are washed out, and the settling solid constituents are heated to approximately 450°C in order to burn any organic constituents that may be left. After cooling, pulverization takes place, and the powder is mixed with an aqueous ammonium-halide solution. For example 1 kg ammonium chloride (NH_4Cl) is dissolved in 13 l of demineralized water, and 1 kg of the powder is mixed with this solution in a mixing vessel 1 by means of a stirrer 2.

This mixture then flows through an electrolysis apparatus. The chief component of this apparatus is a longitudinally divided graphite tube 3 whose halves 31 and 32, which are mechanically joined together again by means of insulating layers but are electrically isolated from each other, serve as electrodes. Instead of using a round, longitudinally divided graphite tube 3 of circular section, two graphite plates 31 and 32 may be joined together by means of insulating parts 33 to form a tube of rectangular section. A valve 14, e.g. a hose clamp, disposed behind the tube 3 allows the rate of flow through the tube 3 to be regulated. This flow rate is adjusted so that the above mixture flows through the electrolytic arrangement in about 4.5 hours at an electrode current of 9 to 14A, for example.

70 The graphite tube is surrounded by a cooling facility 5 which may be a cooling coil as shown in the figure, but also a cooling jacket, and is traversed by the cooling liquid, e.g. cooling water, countercurrently to the mixture in the tube 3. By means of a blow-in pipe 6, air or nitrogen is blown into the tube 3, also countercurrently to the mixture, to prevent the tube halves 31 and 32, which serve as electrodes, from becoming inactivated due to deposition of phosphor particles, sulphur, and cathode deposit.

75 After flowing through the valve 14, the electrolytic products pass through a sieve 7 whose apertures are about 30 μm in diameter and which separates the sulphur and the cathode deposit from the electrolytic products. The residue is collected in a collecting tank 8, the solid constituents 9 sinking to the bottom and being separable by decanting the supernatant liquid. The liquid 10 can be used for one or two additional, like electrolytic processes, while the solid constituents are washed, reheated to about 450°C, cooled down, and pulverized. The powder is then mixed again with an aqueous ammonium-halide solution according to the same recipe and subjected to an electrolytic process of the same kind. Either the same electrolysis arrangement may be passed through again, or a second, like arrangement may follow the first. After decanting, the ammonium-halide solution used in the second electrolysis may be reused, too.

80 The powder obtained after washing and drying is an almost pure red rare-earth phosphor whose impurity level is not higher than that of the red phosphor to be regenerated by known regenerating methods, such as the method disclosed in DT-OS 2,126,893, so that it can be processed by such a method and re-used in

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5	the manufacture of screens, this being possible with and without addition of phosphor straight from the factory, without any deterioration in the quality of the screens. With the method described herein, approximately 95% of the red rare-earth phosphor contained in the sediment of the drain channels of a screen-coding room can be recovered.	c. heating to approximately 450°C, to volatilize further organic constituents;	65
10	Although the method described is more expensive than the prior art methods of regenerating only slightly contaminated rare-earth phosphors, in view of the high price of such phosphors, their recovery from the sediment in the drain channels of a screen-coding room is economically worth while.	d. cooling and pulverising;	
15		e. forming into an aqueous ammonium-halide dispersion;	70
		f. electrolysis during passage between graphite electrodes;	
		g. filtering off sulphur and cathode deposit;	
		h. collecting in a tank, allowing solid constituents to deposit, and decanting the liquid;	
		i. repeating the steps c to h, and	
		j. carrying out one of the known methods of regenerating only slightly contaminated rare-earth phosphors.	75
		3. A method as claimed in claim 1 or 2, wherein the electrodes and the dispersion are cooled during the electrolysis.	80
		4. A method as claimed in claim 3, wherein the cooling takes place countercurrently.	
		5. A method as claimed in any preceding claim, wherein inactivation of the electrodes by deposition of phosphor, sulphur and cathode deposit is prevented by blowing air or nitrogen into the mixture of phosphor and ammonium-halide solution.	85
		6. A method as claimed in claim 5, wherein the air or the nitrogen is blown in countercurrently to the electrolyte.	90
		7. A method as claimed in any preceding claim, wherein the ammonium-halide is ammonium chloride.	95
		8. A method as claimed in any one of the preceding claims, wherein, for the electrolysis steps, the dispersion is passed through a longitudinally divided graphite tube, the two tube halves, being isolated from each other and serving as electrodes.	100
		9. A method as claimed in claim 8, wherein the longitudinally divided graphite tube is surrounded with cooling coils or a cooling jacket.	105
		10. A method of recovering red rare-earth phosphor substantially as hereinbefore described with reference to the accompanying drawing.	
		11. Apparatus for use in the recovery of red rare-earth phosphor, substantially as hereinbefore described with reference to, and as illustrated in the accompanying drawing.	110
		12. Red rare-earth phosphor recovered by a method or apparatus according to any preceding claim.	115
		13. A method of manufacturing colour television tubes including applying an aqueous dispersion containing phosphors to the screen of a television tube to form a coating, removing excess coating dispersion and recovering red phosphor from the	120

removed material by a method or apparatus as claimed in any of claims 1 to 11, and using the recovered red phosphor in a further aqueous dispersion and applying it to the screen of a further television tube in the manufacture thereof.

14. The further television tubes made by the method claimed in claim 13.

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