JOURNAL OF MATERIALS SCIENCE **35** (2000) 3959–3961

Homogeneous coatings of nanosized Fe_2O_3 particles on Y_2O_2S:Eu

J. MERIKHI, C. FELDMANN*
Philips Research Laboratories, Weisshausstrasse 2, D-52066 Aachen, Germany
E-mail: claus.feldmann@philips.com

The red emitting phosphor Y_2O_2S:Eu commonly applied in colour television tubes was pigmented with a thin homogeneous layer of nanosized Fe_2O_3 particles based on a novel coating strategy. In a first step the phosphor was covered with nanosized Fe_3O_4 particles which themselves were prepared by reduction of an Fe(III)-salt with hydrazine. Thereafter, Fe_3O_4 was converted to Fe_2O_3 by heating to 450°C in air. Surface composition and body colour of the corresponding phosphor samples were investigated applying ESCA and measuring diffuse reflectance. The size of the Fe_2O_3 particles as well as the homogeneity of the resulting coating were studied by SEM. Furthermore, the adhesion of Fe_2O_3 particles on the phosphor surface was examined.

1. Introduction

For colour television tubes a reduction of daylight reflectivity is of major importance with respect to an optimal contrast of screens [1]. A significant part of daylight reflection is caused by the luminescent materials which are usually bright white powders. To avoid this effect and thus to improve contrast, the phosphor surface is covered with a pigment. However, the light absorption of pigments is limited by the fact that no light should be absorbed which is emitted by the phosphor itself. As a result, the pigment body colour has to correspond to the colour of light emitted by the phosphor. In case of phosphors for colour television tubes, for instance, blue emitting ZnS:Ag,Al is pigmented with $CoAl_2O_4$ [2, 3] and red emitting Y_2O_2S:Eu with α-Fe_2O_3 [4]. In fact, pigments do absorb part of the emitted light. In terms of contrast, this obvious disadvantage is overcompensated by a reduced daylight reflectivity only if the amount of pigment is controlled precisely [5].

Considering the pigment covering the surface of individual phosphor particles, besides its light absorption an additional requirement has to be taken into account. For production process pigmented phosphors are exposed to mechanical (e.g. stirring or pumping of phosphor suspensions) and chemical forces (e.g. shift of pH). To prevent the pigment from being detached, a sufficient adhesion on the phosphor surface has to be guaranteed. This demand can be fulfilled if non-agglomerated pigment particles significantly smaller than the phosphor grains are deposited as homogeneous as possible on the surface of the latter. In fact, based on phosphor particles 5 to 8 μm in size, pigment particles smaller than 100 nm are required. Former investigations give evidence for the fact that optimal adhesion and homogeneous distribution are achievable if the pigment particles are prepared directly on the phosphor surface by, for instance, homogeneous precipitation of α-FeO(OH), $FeSO_4$ or FeS_2 which themselves are converted into α-Fe_2O_3 by heating [6–9].

In the course of the present study, a novel method to pigment Y_2O_2S:Eu with Fe_2O_3 is described. In a two-step-process the phosphor was covered firstly with nanosized Fe_3O_4 particles which were oxidized in a second step to yield Fe_2O_3.

2. Experimental

2.1. Preparation of nanosized Fe_3O_4 particles

1.68 g $FeCl_3 \times 6H_2O$ (98 %, Aldrich) were dissolved in 50 ml demineralised water. 0.85 g $N_2H_4 \times 2HCl$ (98 %, Aldrich) dissolved in 50 ml water were added and the pH of the solution set to 6.0. Afterwards, the solution was heated to 90°C and the temperature kept 60 min. The resulting deep black suspension was stored in a glass bottle. It contained 0.48 g Fe_3O_4.

2.2. Coating of Y_2O_2S:Eu

10 g Y_2O_2S:Eu (Philips) were suspended in 100 ml demineralised water. The suspension was stirred continuously and its pH set to 6.0 by addition of 0.01 M HCl. Afterwards, 10 ml of the Fe_3O_4 containing suspension were added dropwise. After 1 h of continuous stirring, the suspension was filtered and the residue washed carefully with several portions of water. The coated phosphor was dried 120 min at 120°C in a drying oven and then heated 60 min to 450°C in a tube furnace. During this final treatment the body colour changes from deep grey to red. The preparation yields Y_2O_2S:Eu covered homogeneously with 0.5 wt.-% nanosized Fe_2O_3 particles.

---

* Author to whom all correspondence should be addressed.

2.3. Adhesion test

To test the adhesion of Fe_2O_3 particles on Y_2O_2S:Eu, 0.5 g pigmented phosphor were suspended in 10 ml demineralized water. 2 ml of a polyacrylic acid containing solution (1.0 vol.-% PA30, Rohm & Haas) were added and the suspension stirred continuously 24 h at room temperature. Afterwards, the phosphor was sedimented and the presence or absence of loose pigment checked visually in the stabilised supernatant liquid. In addition, the solid residue was filtered off, washed carefully with water and heated 1 h in air to 450°C to burn out the acrylic acid. Finally, the surface composition of the pigmented phosphor was controlled by ESCA. Altogether, this type of adhesion test simulates conditions of production reliably.

2.4. Electron spectroscopy for chemical analysis (ESCA)

ESCA measurements were carried out with a MICROLAB VG machine. The excitation was performed by an Al-K_α source and a power of 300 W. A spherical sector analyser equipped with a triple channeltron detector was used to collect the photoelectrons. The angle between the detector and the sample was 90°. Photoelectron spectra were recorded for binding energies between 0 and 1200 eV with a step size of 0.6 eV. The analysed spot was about 0.25 cm^2 in size.

2.5. Diffuse reflectance

The diffuse reflectance was measured in an Ulbricht-sphere (double monochromators, 350–800 nm, semi-infinite layer of samples). Spectra were recorded at room temperature, using home-built equipment. $BaSO_4$ was used as reference material.

2.6. Scanning electron microscopy (SEM)

A PHILIPS SEM 525R equipped with a LaB_6 cathode was used for the SEM analysis. The samples were sputtered with gold. The investigations were carried out at room temperature, a voltage of 15 to 25 kV, a spot size of 20 nm and a free working distance (FWD) of 9 to 12 mm.

3. Results and discussion

Based on the reduction of Fe(III)-salts with hydrazine which is known to yield nanosized Fe_3O_4 particles [10, 11], the pigmentation of Y_2O_2S:Eu was carried out according to the following sequence of reactions [12]:

(1) $6\,Fe^{3+} + 2\,N_2H_4 + 8\,H_2O \rightarrow 2\,Fe_3O_4 + N_2 + 2\,NH_3 + 18\,H^+$

(2) $2\,Fe_3O_4 + 1/2\,O_2 \rightarrow 3\,Fe_2O_3$

TABLE I ESCA analysis of uncoated Y_2O_2S:Eu and samples coated with Fe_3O_4 and Fe_2O_3

Sample	Y [at.-%]	S [at.-%]	O [at.-%]	Eu [at.-%]	Fe [at.-%]
Y_2O_2S:Eu (raw material)	34.3	7.1	57.5	1.1	0.0
Y_2O_2S:Eu (coated with 0.48 wt.-% Fe_3O_4)	25.8	6.2	58.6	1.5	7.9
Y_2O_2S:Eu (coated with 0.5 wt.-% Fe_2O_3)	18.4	7.3	64.5	1.4	8.4
Y_2O_2S:Eu (coated with 0.5 wt.-% Fe_2O_3, after adhesion test)	20.1	5.0	65.7	1.2	8.0

Adding a suspension of such Fe_3O_4 particles to a suspension of Y_2O_2S:Eu, both in water, the former adhere almost immediately and completely on the phosphor surface. After phosphor separation, the filtrate was free of Fe_3O_4 particles. Finally, the coated phosphor was heated in air to 450°C in order to oxidize magnetite to Fe_2O_3. Based on the relation between pigment load and optimal contrast in a colour picture tube [5], a total amount of 0.5 wt.-% Fe_2O_3 referred to phosphor weight was applied. Taking an increased light reflectivity of very small pigment particles into account, this pigment load was chosen to be located at the upper limit of the optimal concentration range.

The course of the reaction sequence can be illustrated by ESCA analysis (Table I). Comparing raw Y_2O_2S:Eu and the material coated with Fe_3O_4, in the latter case the concentrations of yttrium and sulfur are decreased whereas the occurrence of iron and an increased oxygen content is to be observed. Both indicates that part of the surface is covered with an iron oxide. In agreement with an oxidation of Fe_3O_4 to Fe_2O_3, the amount of oxygen is increased even further after heating. Measuring the diffuse reflectance of the corresponding samples, the change of body colour becomes visible (Fig. 1). In agreement with its bright white colour, raw Y_2O_2S:Eu has a high reflectivity over the whole range of visible light limited by band absorption in the near UV. If the material is coated with Fe_3O_4 the reflectivity drops tremendously over the whole spectral region investigated. Consequently, the phosphor is greyish. After oxidation of Fe_3O_4 to Fe_2O_3, the reflectivity in the blue and green region of visible light (400–570 nm) is decreased even further. In contrast, it is increased significantly between 570 and 780 nm where red emission of Y_2O_2S:Eu occurs. Now, the body colour has turned to red as it is

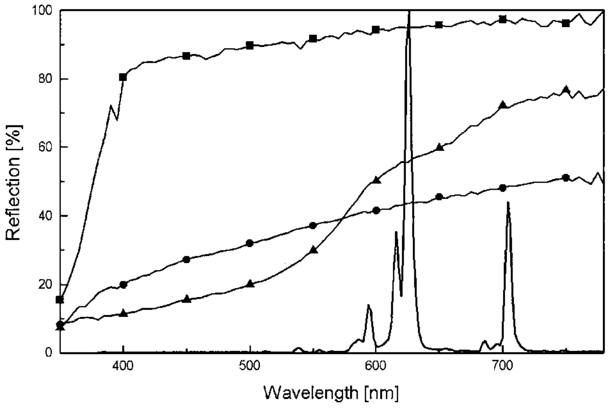

Figure 1 Diffuse reflection of Y_2O_2S:Eu: uncoated (square), coated with 0.48 wt.-% Fe_3O_4 (circle) and coated with 0.5 wt.-% Fe_2O_3 (triangle); emission spectra of Y_2O_2S:Eu added as reference (straight line).

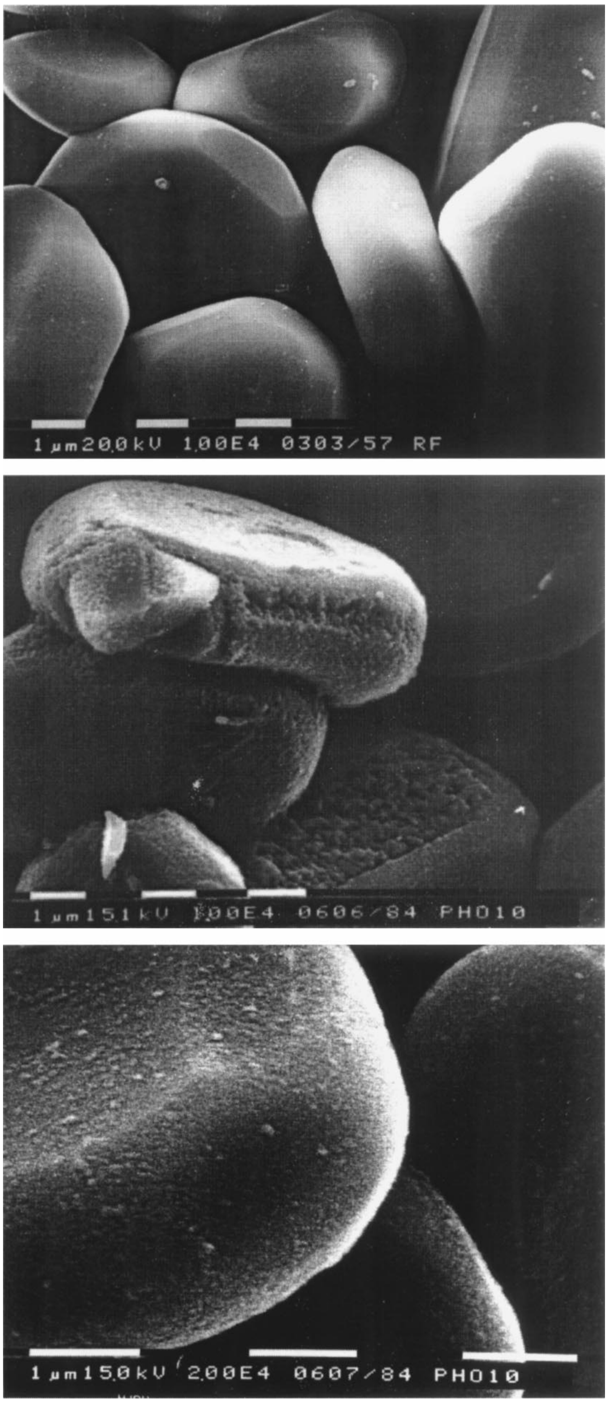

Figure 2 SEM picture of Y_2O_2S:Eu: uncoated (top) and coated with Fe_2O_3 (middle, bottom); (1 : 10000, 1 : 20000).

characteristic for α-Fe_2O_3. Altogether, it is very comparable to pigmented Y_2O_2S:Eu commonly applied in colour television tubes.

SEM pictures of Y_2O_2S:Eu coated with Fe_3O_4 and Fe_2O_3 do not show significant differences. The pigmented phosphor after heating to 450°C is pictured in comparison to Y_2O_2S:Eu raw material (Fig. 2). The phosphor grains turn out to be covered very homogeneously with a thin film of Fe_2O_3 particles 40 to 60 nm in size. To test the adhesion of Fe_2O_3 on Y_2O_2S:Eu, the pigmented phosphor was stirred 24 h in a polymer stabilized suspension. Two facts prove a reliable adhesion of the pigment particles: on one hand, after sedimentation of the phosphor material no loose pigment is visible in the supernatant liquid, on the other hand, it is confirmed by ESCA that the iron concentration on the phosphor surface remains constant before and after the adhesion test (Table I). The strong attractive interaction between phosphor and pigment can be ascribed to the size of the Fe_2O_3 particles. Since they are very small, their contact interface to the phosphor grain is large. Moreover, a condensation of Y-OH groups on the phosphor surface and Fe-OH groups on the magnetite particles can be assumed while heating the material to 450°C [13, 14]. The resulting metal-oxygen bonds between phosphor and pigment as well as between pigment particles strengthen the attractive forces even further.

4. Summary

The red emitting phosphor Y_2O_2S:Eu was pigmented applying nanosized Fe_3O_4 particles as a pigment precursor. Heating the precursor coated Y_2O_2S:Eu in air, magnetite was oxidized to Fe_2O_3. Because of a very limited number of parameters to control, the reaction is easy to perform. The analysis of the surface composition as well as the body colour of the coated phosphor samples allow a view on the course of the reactions.

As a result, Y_2O_2S:Eu was covered homogeneously with Fe_2O_3 particles 40 to 60 nm in size. The red body colour of the pigmented phosphor corresponds to the one characteristic for α-Fe_2O_3. Finally, the pigment adhesion was tested and turns out to be sufficient with respect to conditions similar to real tube production.

Acknowledgements

The authors like to thank W. Czarnojan for ESCA measurements and D. Wädow for measuring diffuse reflectance.

References

1. S. SHIONOYA and W. M. YEN, “Phosphor Handbook” (CRC Press, London, 1999) p. 474.
2. T. MIZUKAMI and C. FUNAYAMA, Patent EP 0 887 123 A2.
3. Y. NAKADA, M. ASADA and K. INOUE, Patent US 4 699 662.
4. J. CHOI, I. JEONG and M. PARK, Patent EP 0 491 406 A1.
5. K. CARL, J. A. M. DIKHOFF, W. ECKENBACH and H. G. JUNGINGER, *J. Electrochem. Soc.* **128** (1981) 2395.
6. B. BOLZ, G. KRÖNES, O. MARZEL and H. WIDMANN, Patent DE 28 34 687.
7. H. MORISHITA, S. NONOGAKI, T. MANABE, S. UCHINO, M. NISHIZAWA, O. SASAYA and Y. TOMITA, Patent DE 29 39 258.
8. K. FRANZ and B. SCHÖNFELD, Patent DE 29 00 209.
9. C. R. RONDA and M. BREDOL, *J. Colloid Interface Sci.* **173** (1995) 328.
10. Y. LI, H. LIAO and Y. QIAN, *Mater. Res. Bull.* **33** (1998) 841.
11. K. S. RANE, V. M. S. VERENKAR, R. M. PEDNEKAR and P. Y. SAWANT, *J. Mater. Sci. Mater. Electron.* **10** (1999) 121.
12. N. N. GREENWOOD and A. EARNSHAW, “Chemistry of the Elements” (Pergamon Press, Oxford, 1984) p. 493.
13. D. MEYERS, “Surfaces, Interfaces and Colloids” (VCH, Weinheim, 1991) p. 405.
14. C. FELDMANN and J. MERIKHI, *J. Colloid Interface Sci.* **223** (2000) 229.

Received 20 October
and accepted 14 December 1999