

New process for the preparation of pigment-coated phosphors on the base of electroacoustic characterization

A.L. Costa^{a,*}, G. Bezzi^b, T.M.G. La Torretta^b, S. Verna^b

^aCNR-IRTEC, Research Institute for Ceramics Technology, Via Granarolo 64, Faenza, I-48018 Italy

^bENEA, New Materials Division- Research Centre, Via Ravegnana 186, Faenza, I-48018 Italy

Received 27 June 2001; accepted 13 October 2001

Abstract

A simple and easily reproducible method for binding pigment particles to phosphor ones was realised, using an heterocoagulation process. An electrokinetic technique was used to measure the ζ potential of phosphor and pigment particles suspensions at different pH in the presence or not of dispersing and binding agents. Starting from the results of these measurements it was possible to optimise the process. This process introduced as binding agent a liquid fatty amine, generally used as liquid anion exchanger and never used before at this purpose, whilst as dispersing agent it was used an ammonium salt of polyacrylic acid. The pigment powder was coagulated over the phosphor powder in a pH region where surfaces had opposite charge, resulting in a stable deposition of pigment on the phosphor particles. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Coating; Phosphors; Pigments; Suspensions; Y_2O_3 ; ZnS; Fe_2O_3 ; $CoAl_2O_4$

1. Introduction

Blue emitting, green emitting and red emitting phosphors particles are widely employed in viewing screens for colour television cathode-ray tubes. In order to improve the emission luminance and the colour contrast these phosphors have to be coated with pigment particles that adsorb wavelengths of visible spectrum not emitted by those phosphors. Many methods for binding pigment particles to phosphors have been developed, most of these involving organic binder systems such as: gelatine and polyvinyl pyrrolidone, PVP,¹ gelatin and gum arabic,² gelatin and casein,³ latex polymers or copolymers, principally of acryl series, having anionic or cationic functional groups.^{4–6} The typical procedure involves:

1. dispersing phosphor particles into an aqueous solution with a latex polymer
2. dispersing pigment particles into an aqueous solution with PVP or other latex polymers

3. mixing the two dispersions
4. collecting the resulting phosphor coated precipitate

The main problem of this process is avoiding flocculation of the phosphor particles and the pigment particles before their adhesion. To achieve this result the slurry pH was varied in order to increase the attractive energy between phosphor and pigment particles.^{7,8} However, no indication regarding the reason for the choice of the best working pH can be deduced by these inventions. Furthermore these methods always involve long and laborious procedures for the dispersion of particles and their adhesion with latex.

In this work an electroacoustic technique was used to investigate dispersive behaviour of phosphors and pigment aqueous slurries through measurements of ζ potential. On the basis of these results interparticle forces were manipulated by controlling the pH of the slurries in order to increase the attractive energy between phosphor and pigment particles. Starting from a phosphor and pigment having opposite surface charges, an heterocoagulation process⁹ was realised and presented as an interesting method for preparing pigment-coated phosphors.

* Corresponding author.

E-mail address: acosta@racine.ra.it (A.L. Costa).

2. Experimental procedure

2.1. Materials

Europium activated yttrium oxysulfide ($Y_2O_2S:Eu$, R-pho) and silver-activated zinc sulfide ($ZnS:Ag$, B-pho), produced in the research laboratories of Ce.Ri.Ve, Venezia, Italy, were used as red and blue emitting phosphors; hematite ($\alpha-Fe_2O_3$, Sicotrans Red K 2915, R-pi) and cobalt aluminate ($CoO.nAl_2O_3$, Sicopal Bleu K 6310, B-pi) both from BASF-ITALIA Cesano M., Italy, were used as red and blue pigments. The measurement of powder particles sizes was made by light scattering (Model N4S, Coulter, Miami, FL) and gave the following results of mean diameter size (μm): R-pho: 7.4, B-pho: 7.1, R-pi: 0.31, B-pi: 0.48. The chosen additives were Duramax D3005 (ammonium salt of polyacrylic acid, Rohm and Haas Company, Philadelphia, USA) for phosphors, Sokalan PA 110S (polyacrylic acid, BASF-ITALIA, Cesano M, Italy) and Amberlite LA-2 (*N*-lauryl-*N*-trialkylmethylamine, Rohm and Haas Company, Philadelphia, USA) for pigments. Concentration of additives is expressed in wt.% on a dry powder basis. The pigment coating on the phosphor powder surfaces was checked by SEM analysis coupled with energy-dispersive-spectrometry, EDS (SEM Cambridge Stereoscan MK3, Cambridge, U.K.).

2.2. Electroacoustic analysis

The electroacoustic characterisation of powder dispersions was made by Acoustosizer (Colloidal Dynamics, Sydney, Australia). The electroacoustic effect measured is the ESA (electrokinetic sonic amplitude) effect referred to the sound wave generated when an alternating electric field is applied to a colloidal suspension. The ESA signal gives information on the dispersive state of the dispersion, being proportional to the dynamic mobility of the particles and as consequence to their electrokinetic potential (ζ potential¹⁰). The acoustosizer measures the ESA response of well-dispersed particles over a range of 13 frequencies (ESA spectrum). The software associated with the acoustosizer¹¹ derives, from the ESA response, the dynamic mobility spectrum and extracts reliable values of ζ potential and size on the basis of a mathematical model developed by O'Brien.^{12,13} Assuming a log-normal distribution of particle sizes, it is defined a mass-averaged mobility and the ζ potential together with particle size distribution are adjusted to give the best fit to the measured mobility spectrum. When the fit error was too high (system far from the ideality), we reported the dynamic mobility magnitude at an intermediate frequency (1.6 MHz) to estimate the sign of the surface charge.

Temperature, pH and conductivity probes detected temperature, pH and conductivity of the suspension

during the measurement. A potentiometric titration software allowed the addition of acid or base according to pH increments set in the experimental setup; a concentration titration software governed the addition of the amount of dispersant. In both cases an equilibrium delay time (two minutes) before each measurement was set. Automatic titration software was used to measure ζ potential as a function of pH between two fixed points; if necessary, the starting pH was adjusted to basic conditions (pH = 9/10) and then decreased until acid conditions (pH = 2), in order to check the point of zero ζ potential termed pHiep. 1 M KOH and 1 M HCl (Carlo Erba) were used to set pH. The automatic concentration titration software was used to measure ζ potential of red phosphor versus amount of Duramax added, in order to determine the best amount of dispersant required. In the graphs of ζ potential it is always reported the conductivity curve, in order to screen ionic strength.

The slurries were prepared at an electrolyte strength of 10 mM KCl (Merck), with the concentrations summarised in Table 1.

The suspensions were prepared by ball milling the slurry of powder and water with 1 : 1 by weight zirconia grinding media (5 mm diameter) for about 3–4 h and for 15–18 h when additives were added. All the suspensions were placed in the Acoustosizer sample holder, stirred and allowed to thermally equilibrate at 25 °C.

2.3. Coating

The coating process was applied in the same way to red and blue phosphor, the only difference was the pH set for the heterocoagulation:

- preparing an aqueous dispersion of phosphor particles using Duramax D-3005 as dispersing agent
- preparing an aqueous dispersion of pigment adding Amberlite LA-2 as binder agent
- uniformly mixing the two dispersions, adding 1M HCl to adjust pH to acid values (2.5)
- separating the liquid, washing, dewatering and drying the precipitate

Table 1
Preparation condition of suspensions for electroacoustic characterization

Sample	Powder (wt.%)	Additive (wt.%)
1	Phosphor (15)	Duramax (0.5) ^a
2	Pigment (0.5)	Sokalan (2) ^b
3	Pigment (0.5)	Amberlite (100) ^b

^a Wt.% calculated on phosphor amount.

^b Wt.% calculated on pigment amount.

2.3.1. Pigment dispersion

Pigment (0.5 g) was suspended in distilled water in the presence of the same quantity of Amberlite LA-2 (0.5 g). Pure water was added until the weight of suspension is 100 g (pigment 0.5 wt.%, Amberlite 100 wt.% on pigment). The suspension was ball milled for 12 h.

2.3.2. Phosphor dispersion

Phosphor (7.5 g) was suspended in distilled water in the presence of Duramax D3005 (0.04 g). Pure water was added until the weight of suspension was 50 g (phosphor 15 wt.%, Duramax 0.5 wt.% on phosphor). The suspension was ball milled for 3 h.

2.3.3. Coating process

Ten grams of phosphor suspension was subjected to dispersion by means of an agitator and 0.9 g of pigment suspension was slowly added (0.3 g of pigment for 100 g of phosphor). Then the mixture was adjusted to pH 2.5 for red phosphor and to pH 4/5 for blue phosphor and agitation was stopped. The precipitate formed was separated by decantation from the liquid that results limpid water without pigment particles suspended. Cleanings were carried out with a diluted HCl solution and the precipitate was dried for 1 h at 100 °C.

3. Results and discussion

3.1. Electrokinetic measurements

Figs. 1 and 2 show the dynamic mobility magnitude of red phosphor and pigment without additives as a function of pH. The pigment powder holds a positive surface charge in the whole pH range tested while phosphor has a p_Hiep at about pH 7. Nevertheless both suspensions are not stable without adding additives and reliable data of ζ potential can not be detected. In these conditions it's not possible handling the slurries. Fig. 3 shows the ζ potential of red phosphor as a function of Duramax D3005 added. A little amount of dispersant (0.25 wt.%) is sufficient to negatively charge the surface of phosphor powder (about -40 mV). It was not surprising that an anionic polyacrilate showed a good affinity for sulfide particles dispersed in water as well as for oxides^{14,15}. In fact these particles result surrounded by sulfur-hydroxy species¹⁶ that show a reactivity similar to hydroxide groups surrounded hydrated oxides surfaces. The absolute value of ζ increases up to Duramax concentration about 3 wt.%, corresponding to a complete particles coverage. Nevertheless, the ζ potential reached at Duramax concentration 0.5 wt.% (about -50 mV) is sufficient to ensure a good stability to the dispersion. It was verified that 0.5 wt.% of Duramax is sufficient to stabilise the suspensions of red and blue phosphor too. Figs. 4 and 5 show the ζ potential of red and blue

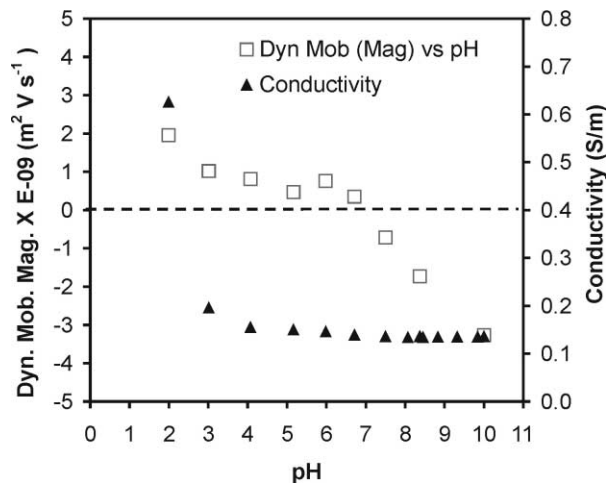


Fig. 1. R-pho: dynamic mobility magnitude vs pH.

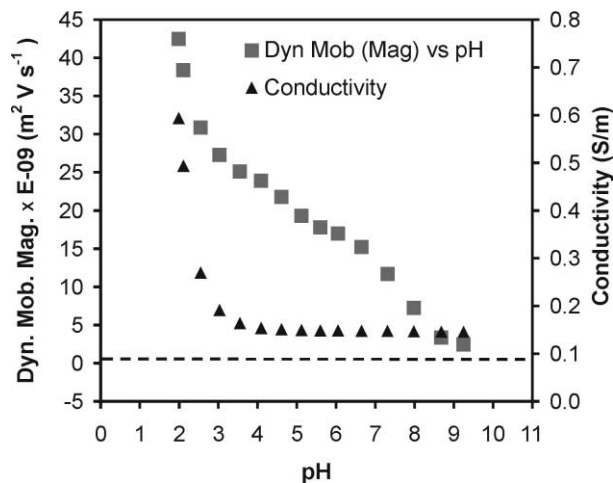


Fig. 2. R-pi: dynamic mobility magnitude vs pH.

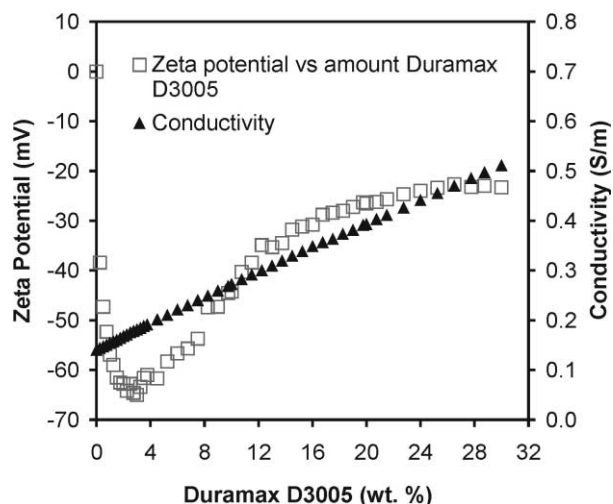


Fig. 3. R-pho: zeta potential vs amount of Duramax D3005 (wt.%).

phosphors plus Duramax as a function of pH. In both cases ζ potential remains negative over the whole pH range tested, decreasing in magnitude with decreasing pH, from -80 mV for red phosphor and -30 mV for blue phosphor up to $-10/-5$ mV. The acid-base behaviour of these surfaces is depending on the OH groups adsorbed on when powders are dispersed in water. The sharp decreasing of ζ potential starting at pH 6 for red phosphor and at pH 10 for blue phosphor, indicates a different reactivity of groups adsorbed into the surfaces, even if both powders reach very low ζ potential values at acid pH ($-5/-10$ mV, $\text{pH} < 3$). Figs. 6 and 7 show the ζ potential of red and blue pigments plus Amberlite as a function of pH. At starting basic pH (about 9) the pigments surfaces result negatively charged, indicating an excess of MO^- sites.¹⁷ The Amberlite LA-2 is a liquid fatty amine usually used in a salt form as liquid anion exchanger; an example is indicated in the following equation:

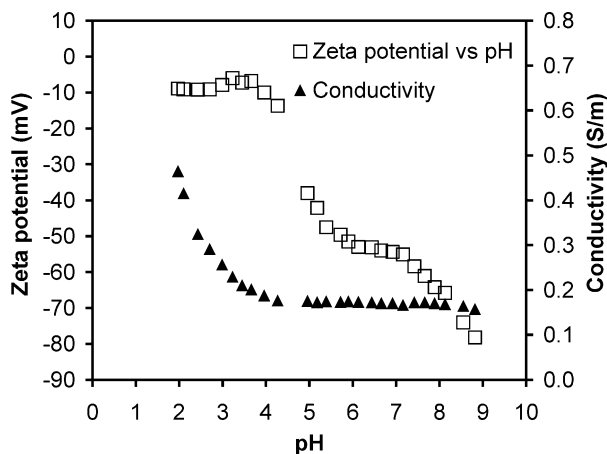
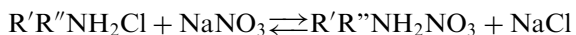


Fig. 4. R-pho with Duramax D3005 (0.5 wt.%): zeta potential vs pH.

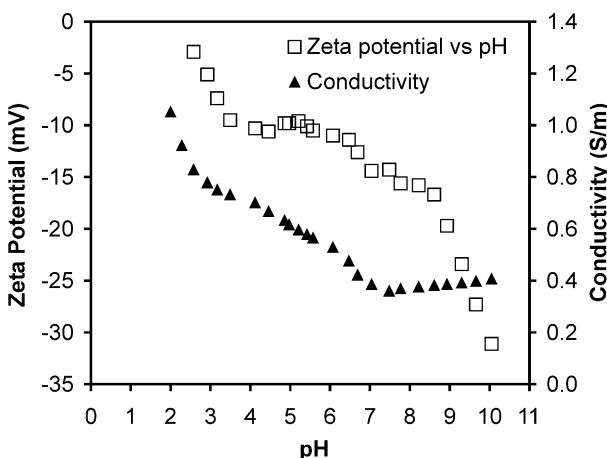


Fig. 5. B-pho with Duramax D3005 (0.5 wt.%): zeta potential vs pH.

The strong interaction of Amberlite with MO^- sites ensures a good colloidal stability to the powder up to acid pH, where the powders result positively charged, as a consequence of steric repulsion due to the long chain ($\text{C}_{12}\text{H}_{25}$) of lauryl group. A further study of Amberlite interaction mechanism with pigments surfaces is still on progress. Blue pigment powder reaches positive values of ζ potential at higher pH than red pigment (pHiep 7 versus 5) indicating a different acid-base reactivity of MOH groups. Fig. 8 shows the ζ potential of red pigment plus Sokalan versus pH. This additive was chosen because suggested by the pigments suppliers as optimum dispersing agent for this kind of powders in water. It was added in a quantity of 2 wt.% in according to technical information of the product. It can be seen that pigment surfaces reacts with Sokalan resulting negative in the whole pH range examined. This result is good for the dispersing aim of the system but it is not good for the heterocoagulation process having pigment and phosphor particles the same negative charge in the whole pH range examined. Table 2 summarises the

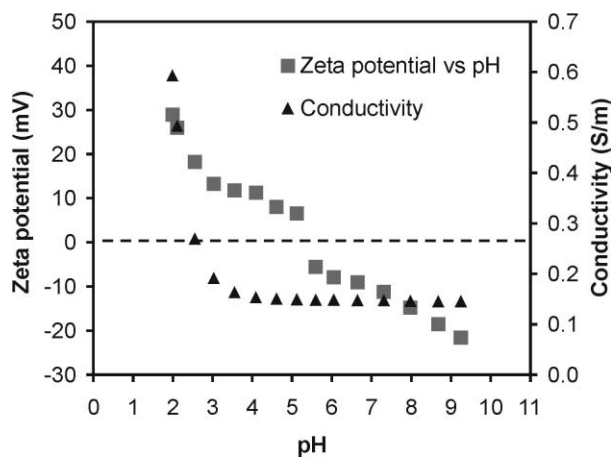


Fig. 6. R-pi with Amberlite LA-2 (100 wt.%): zeta potential vs pH.

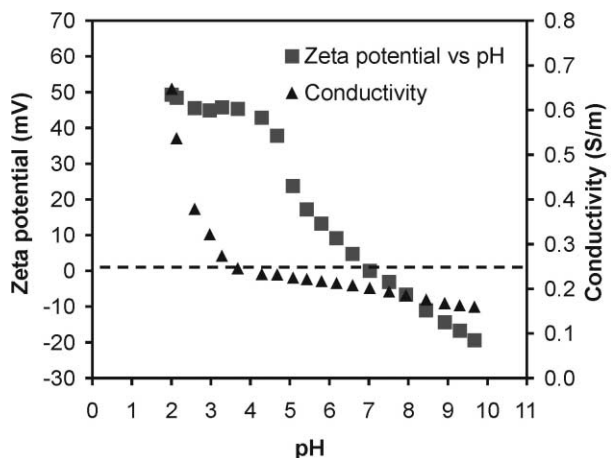


Fig. 7. B-pi with Amberlite LA-2 (100 wt.%): zeta potential vs pH.

Table 2
Electroacoustic properties

Powder	Additive	pH	ζ Potential (mV)	pHiep
Red phosphor	–	8.0	Around 0 ^a	7.1 ^b
	Duramax D3005	8.8	–78.2	< 2
Red pigment	–	7.2	+15 ^a	> 10
	Amberlite LA-2	9.2	–21.6	5.4
	Sokalan PA 110S	4.8	–32.9	< 2
Blue phosphor	Duramax D3005	7.2	–24.2	< 2
Blue pigment	Amberlite LA-2	9.7	–19.4	7.0

^a Values affected by big fit errors ($\geq 40\%$).

^b pHiep determined when dynamic mobility magnitude = 0.

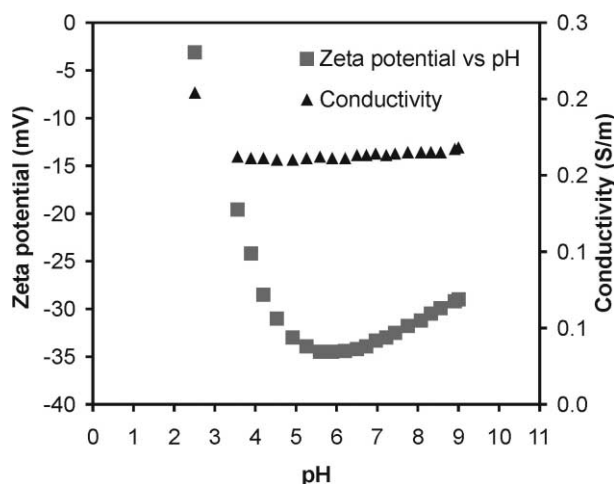


Fig. 8. R-pi with Sokalan PA 110S (2 wt.%): zeta potential vs pH.

values of pH, ζ potential and isoelectric point for phosphors and pigments suspensions in the presence or not of additives.

3.2. Coating

The first attempt of coating was made adding red pigment suspension to red phosphor plus Duramax one taking into account that red phosphor plus dispersant and pigment have opposite charge in the whole pH range tested, nevertheless in this condition the pigment suspension is not stable and the pigment flocculates separately from phosphor. In order to achieve the heterocoagulation of the two particles is necessary adding Amberlite LA-2 to pigment suspension and decreasing the pH up to 2.5, in a region where phosphor and pigment have opposite charges. At this pH the phosphor particles have a ζ potential close to zero and thanks to their dimension (about 7 μm regarding pigment dimension of about 0.5 μm) they quickly precipitated, dragging along the binded pigment particles. In this way a precipitate is instantaneously formed, simply separated by decantation, washed and dried. The precipitate results being phosphor firmly coated by pigment. The

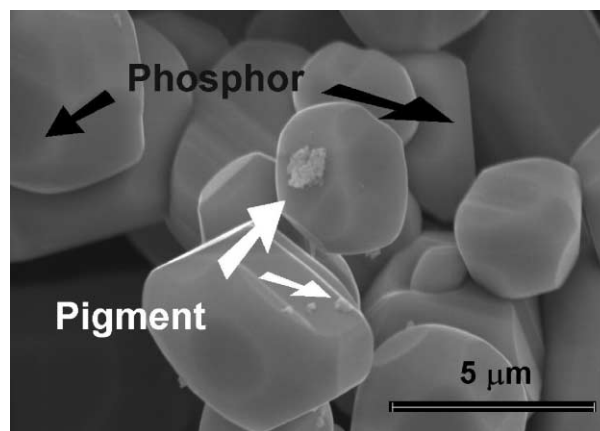


Fig. 9. SEM morphology of pigment-coated red phosphor particles.

SEM analysis coupled with EDS of coated phosphor (Fig. 9) shows pigment particles binded over some phosphor particles coherently with the respective concentrations. The same process was repeated for blue phosphor and pigment leading to the same results. Even though the pH range where blue phosphor and pigment plus additives have opposite charge starts from higher pH in comparison with red phosphor and pigment ($\text{pH} \cong 7$ as regard $\text{pH} \cong \text{pH} 5$), the heterocoagulation process was realised at the same acid pH in order to ensure the best dispersion to the whole system.

4. Conclusion

A process for the dispersion and adhesion of pigment particles to phosphors (working pH, type and amount of additives) was realised, on the basis of electrokinetic characterisation of aqueous slurries of phosphors, pigments and additives. The analysis of ζ potential versus pH allowed the identification of best dispersing conditions together with the pH regions where phosphors and pigments had opposite surface charges. The never used before, as binding agent, Amberlite allowed pigment particles to adhere uniformly to the surface of phosphor without being accompanied by flocculation phenomena.

References

- Lipp, S. A., *Image Display Employing Filter Coated Phosphor Particles*. US Patent 3886394, 1975.
- Kanda, K., Kotera, N., Murakami, S., Yoshida, T., Eguchi, S., Hatsumi, T., Iwasaki, K. and Iwamoto, I., *Pigment Coated Phosphor and Process for Manufacturing the Same*. US Patent 4152483, 1979.
- Kim, U., *Red Pigment Coated Phosphor and Process for Manufacturing Said Phosphor*. US Patent 5213894, 1993.
- Lozier, G. S. and Branin, P. B., *Method for Preparing Filter-Coated Phosphor Particles*. US Patent 4049845, 1977.
- Oba, Y., Kano, T., Hayashi, M., Takada, H., Kanda, K. and

- Eguchi, S., *Process for Producing Pigment-Coated Phosphors*. US Patent 4219587, 1980.
6. Wolfe, R. W., *Process for Binding Pigment Particles to Phosphor Particles*. US Patent 4853254, 1989.
 7. Byler, W. H. and Mattis, J. J., *Coated Phosphors*. US Patent 3875449, 1975.
 8. Jeong, J., *Process for Preparation of Pigment Coated Phosphor*. US Patent, 5077088, 1991.
 9. Bleier, A. and Westmoreland, C. G., Effects of pH and particle size on the processing of and the development of microstructure in Alumina-Zirconia Composites. *J. Am. Ceram. Soc.*, 1991, **74**(12), 3100–3111.
 10. Lyklema, J., Structure of the solid/liquid interface and the electrical double layer. In *Solid/Liquid Dispersions*, ed. Th. F. Tadros. Academic Press, London, 1987, pp. 63–90.
 11. Rowlands, W. N. and O'Brien, R. W., The dynamic mobility and dielectric response of kaolinite particles. *J. Coll. Interface Sci.*, 1995, **175**, 190–200.
 12. O'Brien, R. W., Electro-acoustic effects in a dilute suspension of spherical particles. *J. Fluid. Mech.*, 1988, **190**, 71–86.
 13. O'Brien, R. W., The electroacoustic equations for a colloidal Suspension. *J. Fluid. Mech.*, 1990, **212**, 81–93.
 14. Davies, J. and Binner, J. G. P., The role of ammonium polyacrylate in dispersing concentrated alumina suspensions. *J. Eur. Ceram. Soc.*, 2000, **20**, 1539–1553.
 15. Tang, F, Yu, L., Huang, X. and Guo, J., Characterization of Adsorption and distribution of polyelectrolyte on stability of nano-zirconia suspensions by auger electron spectroscopy.
 16. Prestidge, C. A. and Rowlands, W. N., Electroacoustic measurements of sulfide minerals particles. *Minerals Engineering*, 1997, **10**, 1107–1118.
 17. Costa, A. L., Galassi, C. and Greenwood, R., α -Alumina–H₂O interface analysis by electroacoustic measurements. *J. Coll. Interface Sci.*, 1999, **212**, 350–356.