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Keywords

homogeneity, monitoring, method, ink

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A Method for Monitoring Ink Homogeneity

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Abstract
An important concern when developing new inks containing novel, bulk, solid-state additives is to ensure
consistency during the printing process. In particular, the additives should not build up on the rollers, blan-
kets or plates during printing. In this work we describe a method for detecting such events and quantitatively
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Keywords
Ink, homogeneity, nanoparticle, luminescence

1. Introduction

A key challenge in formulating new inks containing large proportions of bulk addi-
tives, such as colour-shifting platelets, is to ensure homogeneity in the components
present. This is particularly critical during the actual printing process when local in-
homogeneity may lead to significant degradation of print quality, especially during
extended printing runs. Non-homogeneity of this type may arise because of com-
ponent separation during periods when the ink is left to stand (prior to printing).
Alternatively, it may arise when key components of the ink selectively and strongly
adhere to the ink rollers, ink-transfer blankets, or printing plates used in commer-
cial processes like flexographic or offset printing. In that case, the ink mixture is
destabilized by the printing process itself, leading to poor printing quality and even
potential damage to the surfaces involved in ink deposition. At the present time no

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convenient method exists to detect such events, nor to monitor the homogeneity of an ink during printing (although on-line monitoring systems for colour quality and, therefore, also for ink homogeneity, have been developed) [1].

Inorganic luminescent materials have attracted significant attention since the 1940's. They currently find application, *inter alia*, in numerous display and lighting materials [2]. Amongst the most well-known of these are the yttrium vanadates (YVO_4), which have been used to host various inorganic rare-earth (RE) ions. When doped with Eu^{3+} or Dy^{3+}, the resulting matrices display distinctive photoluminescent emissions. These emissions can be readily detected and their relative intensities can be accurately compared using standard fluorescence spectrometers. Recent advances have seen the synthesis of such materials in nanoparticulate form, i.e., as solid materials whose particle size falls within the nanometre range (1–1000 nm). Such materials are sufficiently small that they may be readily incorporated within most standard printing inks.

In this work we describe a method for monitoring the homogeneity and consistency of inks during commercial printing processes. The method involves incorporating two luminescent nanoparticles in pre-determined amounts into an ink and then monitoring changes in their relative emission intensities during printing.

2. Experimental Section

2.1. Materials

The oxides Y_2O_3, Eu_2O_3 and Dy_2O_3 were obtained from Aldrich, Australia in 99.99% purity. NH_4VO_3 (99.0%), $FeCl_3 \cdot 6H_2O$ (98.0%) and citric acid monohydrate (96.0%) were obtained from Ajax Chemical, Sydney, Australia. $FeCl_2 \cdot 4H_2O$ (99.0%), tetraethyl orthosilicate (TEOS) and poly(ethylene glycol) 6000 (average molecular weight 6000–75000) were obtained from BDH.

2.2. Synthesis of Rare-Earth Doped Yttrium Vanadate

Rare earth (Dy^{3+}, Eu^{3+} and Dy^{3+}/Eu^{3+}) doped yttrium vanadates were synthesized using the Pechini sol–gel process [3, 4]. The doping concentration of the rare earths was 5 mol% that of Y^{3+} in the yttrium vanadate [3, 4]. Stoichiometric weights of Y_2O_3, rare earths (Eu_2O_3 or Dy_2O_3) and NH_4VO_3 were dissolved in dilute nitric acid with heating. Further citric acid in water–ethanol (v/v = 1:7) mixture was added to the aforementioned solution. The molar ratio of the metal ions to citric acid was 1:2. Poly(ethylene glycol) (PEG) was added to the final solution having concentration 0.08 g/ml [5]. The solution was heated to dryness and the dried samples were sintered at 800°C with a heating rate of 5°C/min and held at 800°C for 2 h. The sintered samples were then ground. EDX measurements confirmed the presence of the doping element. Figure 1 displays the EDX spectrum of YVO_4:Eu.
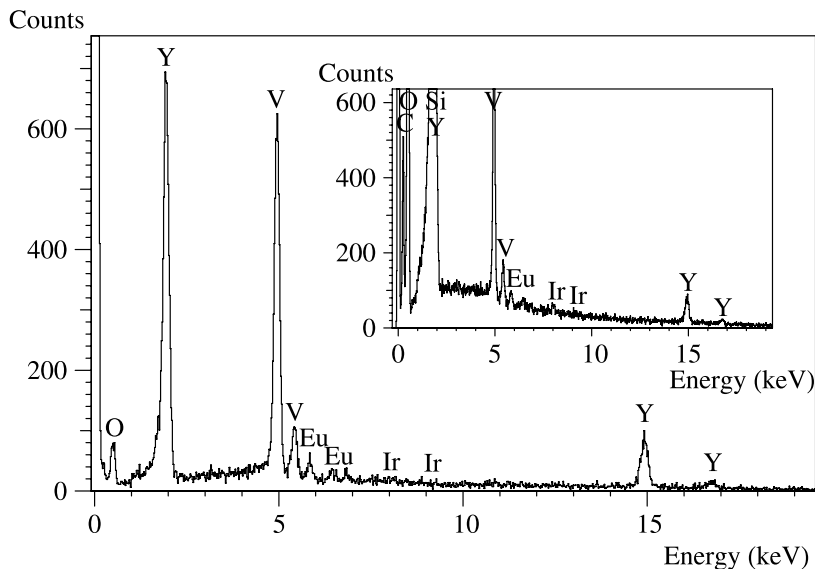
Figure 1. EDX spectrum showing the presence of Eu in Eu^{3+} doped YVO_4 nanoparticles. The inset depicts a close-up of the baseline.

2.3. Synthesis of Silica-Encapsulated Particles

Silica-encapsulated particles were synthesised by modifying the well-known Stöber synthesis [6]. In the Stöber synthesis, silica spheres are prepared by the hydrolysis of TEOS (tetraethylorthosilicate) in an ethanol solution containing water and ammonia [6, 7]. In a typical synthesis, a colloidal dispersion of the yttrium vanadates, TEOS, water and ammonium hydroxide was prepared. The colloidal dispersion was added to the ethanol solution and stirred vigorously at room temperature for 2–3 days. The dispersion with silica-encapsulated particles was separated by centrifugation (3000 rpm).

2.4. Ink Formulation and Printing Studies

Samples of YVO_4:Dy, YVO_4:Eu and YVO_4:Dy, Eu were added in the ratios and weight percentages cited in Table 1 into a standard, commercial offset ink (ca. 1 g) prior to printing. Mixing was performed by hand using a spatula (typically 3 min vigorous hand-mixing). The base ink used was MX 6010/2.5 Matrix Eco PMS Transparent White, manufactured by DIC Colortron, Heatherton, Victoria, Australia. The resulting inks were then printed on test strips using an IGT Printability Tester AIC2-5 machine (IGT Testing Systems, Keienbergweg Amsterdam, the Netherlands) located within the Department of Chemical Engineering at Monash University, Australia. The machine was maintained at a constant temperature of 22°C with relative humidity 50%. The weight per unit area of ink deposited or Grams per Square Metre (GSM), was calculated by weighing the test strips before and after printing, and taking into account the printed area. Non-fluorescent paper

Table 1.

Comparison of the relative ratios of emission intensities of inks prepared for this study. Data in the right-hand column for each of Ink 1 and Ink 2 are the optimum obtained after thorough mixing of the individual components in the ink

Paper type[a] (GSM)[b]	% Yttrium vanadate in ink by weight	Ratio of emission intensities (Dy:Eu)			
		Ink 1		Ink 2	
		YVO_4:Dy, Eu	YVO_4:Dy + YVO_4:Eu	YVO_4:Dy, Eu	YVO_4:Dy + YVO_4:Eu
Glossy	1	0.1422	0.1422	0.1351	0.1351
(2 GSM)	2	0.1422	0.1422	0.1351	0.1349
	3	0.1422	0.1423	0.1351	0.1346
Matt	1	0.1422	0.1423	0.1351	0.1348
(3 GSM)	2	0.1422	0.1425	0.1351	0.1348
	3	0.1422	0.1424	0.1351	0.1348

[a] Non-fluorescent paper was used throughout.
[b] GSM Grams of ink per square metre.

was used in all tests, either with a glossy or a matt finish. For the matt paper, printing was undertaken at 3 GSM ink thickness. To compensate for reflection by the glossy paper, printing aimed to achieve a lower target of 2 GSM in that case. The data shown in Table 1 are for printed samples within 5% of the depicted GSM values. Even substantial variations in the ink GSM did not significantly alter the data shown in Table 1 (between 1.0–4.0 GSM). As can be seen, the glossy or matt finish of the paper also did not make a significant difference in the measured data.

## 2.5. Characterization Techniques

The test strips were studied, after air drying, using fluorescence spectroscopy, which was performed with a Perkin Elmer LS50B spectrometer. Online monitoring in real time was carried out using an Ocean Optics USB2000 microspectrometer equipped with a xenon lamp and fibre-optic cable. Identical data were obtained for the online and the static monitoring methods. Data were taken at random positions on the test strips and found to be highly consistent in the ratio of emission intensities. Table 1 lists the relative emission intensities of the yttrium vanadates for the printed test strips.

3. Results and Discussion

Nanoparticulate lanthanide (Dy^{3+}, Eu^{3+} and Dy^{3+}/Eu^{3+}) doped yttrium vanadates were synthesized using the Pechini sol–gel process [8, 9]. Grinding of the resulting particles was followed by coating with a thin layer of silica (Scheme 1) to protect the underlying vanadate lattice from interactions with the surrounding environment that could lead to quenching of the emission when incorporated in an ink.
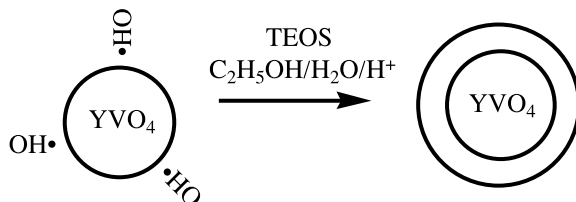
Scheme 1. Schematic representation of the preparation of composite, silica-coated, doped yttrium vanadates.
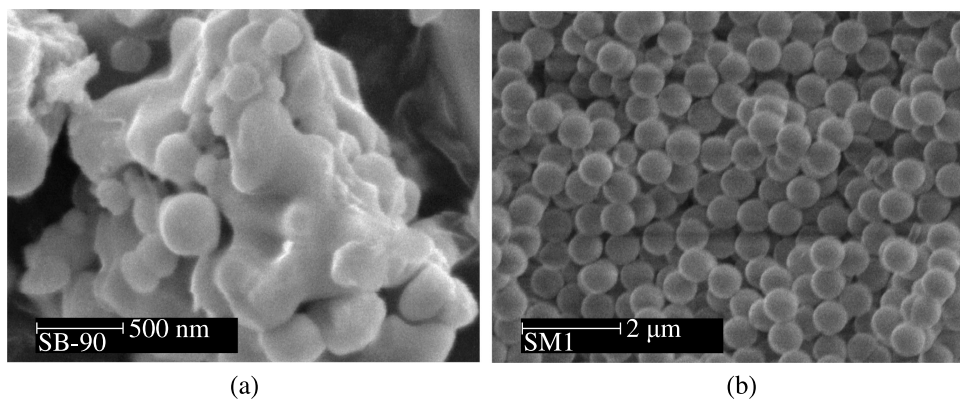
Figure 2. Scanning Electron Microscope images of YVO_4:Eu nanoparticles: (a) after initial sintering and (b) after subsequent grinding and coating with a silica layer (as described in the experimental section).

Figure 2(a) shows an SEM micrograph of the YVO_4:Eu nanoparticles after sintering at 800°C for 2 h. Figure 2(b) shows the particles after coating with silica. As can be seen, they are highly regular spherical particles of average size ca. 800 nm. Figure 3 shows the emission and excitation spectra of the Eu-doped nanoparticles (YVO_4:Eu). As can be seen, a characteristic Eu line emission is produced at 618 nm. The corresponding YVO_4:Dy nanoparticles similarly display a characteristic Dy^{3+} line emission at 575 nm. The mixed Dy^{3+}/Eu^{3+} nanoparticles (YVO_4:Dy, Eu) produce corresponding emissions at both 575 nm and 618 nm. The intensity of these emissions was normalized against a standard sample whose emission intensity was arbitrarily set at unity.

For the printing experiments, two different mixed Dy/Eu yttrium vanadates (YVO_4:Dy, Eu) were prepared with different ratios of emission intensities for the Dy and Eu components. In the first such mixed nanoparticle, the Dy:Eu emission ratio was 0.1422. In the second material, the ratio was 0.1351. When these materials were added to the inks immediately prior to printing, the test prints consistently displayed the above ratios of emission intensities, regardless of changes in the conditions employed. Thus, when the YVO_4:Dy, Eu with intensity ratio 0.1422 was added (Ink 1 left column, in Table 1), the ratio effectively remained constant despite variations in: (i) the loading level of the materials in the ink (1–3% by weight),
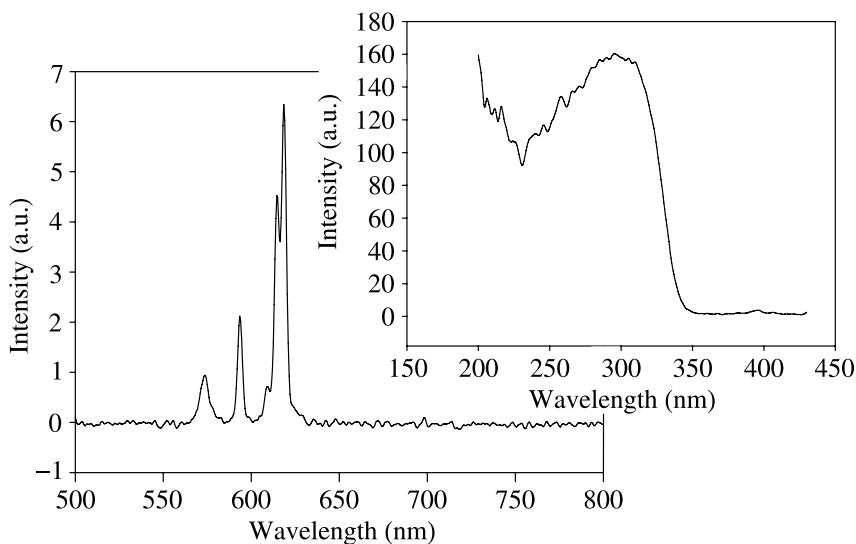
Figure 3. Emission spectrum of Eu^{3+} doped YVO_4 nanoparticles (silica-coated). Inset: their excitation spectrum.

(ii) the type of paper used (glossy or matt) and (iii) the weight of ink deposited per unit area during printing (2–3 GSM). This was also true for the YVO_4:Dy, Eu which displayed an intensity ratio 0.1351 (Ink 2 left column, Table 1). Thus, by incorporating, in a fixed ratio, both the Dy and Eu into the yttrium vanadate matrix and then coating this with a thin silica shell, the relative intensities of the two components were fixed and remained invariant when incorporated into inks. The ratio of the emission intensities remained unchanged even with relatively large variations in the printing conditions.

We then examined whether the individual YVO_4:Dy and YVO_4:Eu could replicate these ratios as carefully weighed mixtures of two separate materials were introduced into inks. We found that if the individual yttrium vanadates were mixed into the inks thoroughly, identical ratios of emission intensities could be achieved. That is, carefully weighed and thoroughly mixed combinations of YVO_4:Dy and YVO_4:Eu could replicate, in all respects, the inks containing YVO_4:Dy, Eu. Thus, as shown in Table 1 (Ink 1 right column), a mixture of YVO_4:Dy and YVO_4:Eu could, upon thorough mixing, yield an intensity ratio of 0.1422–0.1425 under comparable circumstances to those employed for YVO_4:Eu, Dy with an intensity ratio of 0.1422. Similarly, a mixture of individual YVO_4:Dy and YVO_4:Eu could yield an intensity ratio of 0.1346–0.1351 under comparable circumstances to that used for YVO_4:Eu, Dy with the intensity ratio 0.1351 (Ink 2 right column, Table 1).

Any inhomogeneity in these mixed inks, however, caused dramatic, non-linear fluctuations in the ratios of emission intensities. This can be understood from the fact that when a fixed ratio by weight of the individual YVO_4:Dy and YVO_4:Eu is used, then an excess of one particle in one part of the ink must necessarily be

matched by an equivalent shortage of that particle in another part of the ink. Thus, a particular intensity ratio can only be achieved if the ink is near-perfectly homogeneous. In effect, when the emission intensities of two separate materials within the ink are compared relative to each other and not to the emission intensity in another part of the ink, then this is necessarily an extremely sensitive measure of the homogeneity of the ink (since an inconsistency in one part of the ink must be matched by a compensating inconsistency in another part). The extent of inhomogeneity is, moreover, readily observed and measured using a fluorescence spectrometer. This includes a spectrometer adapted with a fibre optic head for real-time monitoring during an extended printing run.

This test provides a convenient means of systematically optimizing new ink formulations, particularly those involving the addition of new bulk additives like colour-shifting platelets, or microscopic polymer or ceramic identifiers, to existing commercially-available inks. In such applications, one of the yttrium vanadates would typically be thoroughly mixed into the commercially-available base ink, while the other is physically attached by static electrical or other means to the new additive. The extent to which the additive is homogeneously mixed within the base ink can then be monitored and quantitatively measured before and after printing.

4. Conclusions

We have demonstrated a novel means of quantitatively monitoring the homogeneity and consistency of new ink mixtures during printing processes. This method involves the use of mixtures of coated, fluorescent nanoparticles of fixed emission intensities. Changes in the ratios of the emission intensities during the printing process are indicative of problems in maintaining a fixed homogeneity and rate of deposition of the ink. The emission intensities can be monitored online and in real time during extended printing runs, by the use of a fluorescence spectrometer equipped with a fibre optic head. The new technique has possible utility when developing new ink mixtures containing large proportions of bulk, particulate additives.

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