



## Dye/Clay intercalated nanopigments using commercially available non-ionic dye

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### ABSTRACT

Two non-ionic azo dyes: solvent yellow 14 (SY14) and solvent red 24 (SR24), and one non-ionic disperse dye: dispersed red 60 (DR60) were chemically modified into their respective cationic species, which were then subsequently ion-exchanged with Na<sup>+</sup>-montmorillonite in an acidic medium. The dye-intercalated montmorillonite was then centrifuged, dried and milled to prepare the pigment particles. X-ray diffraction studies on the pigments showed an increase in the basal spacing in the clay layers for the SY14 and DR60 based pigments NP14 and NP60 respectively, confirming intercalation of the dyes within the clay layers giving rise to a nano-structured system. The XRD pattern of the SR24 based pigment NP24 showed a diffused shoulder with a truncated peak, suggesting the possibility of a delaminated structure after adsorption of the dye. Due to the nano-structured morphologies, these pigments were classified as nanopigments. Thermogravimetric analysis showed different thermal stabilities for different nanopigments compared to the respective original dyes: an improvement in case of NP14, no change for NP24, and an apparent deterioration for NP60. The nanopigments were subsequently mixed with polypropylene to produce coloured specimens. Bleeding tests on these coloured specimens showed a reduction in leaching in turpentine.

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### 1. Introduction

Both pigments and dyes are widely used as colourants for plastics. Dyes offer a wide range of colours, in combination with transparency, as they are dissolved in polymer [1]. This is however a cause of their disadvantage, as the mobility of dye molecules allows greater rate of migration and degradation, in comparison to pigments which are solid particles dispersed into the polymer matrix. Nevertheless, it is considered beneficial to replace some of the existing pigments (especially those based on heavy metals) with organic dyes or hybrid pigments based on dyes [2].

The idea of incorporating dyes into inorganic materials is not new [3]. Many commercial “Lake Pigments” were made by precipitating dyes with inorganic substrates [4]. If the inorganic substrate is a smectite clay or layered silicate, the most effective pathway was found to be using the ion-exchange process (Gemeay, 2002) [5]. For that reaction, the dye must exist in a cationic form, which is the case with basic or cationic dyes. Examples for that are intercalated products of Rhodamine dyes (Rhodamine B, Rhodamine 6G) with hectorite [6], montmorillonite [7–10], and other smectite clays [11–13]. Other basic dyes were also utilised, such as

methylene Blue [14,15]. Majority of the research has focused on describing the influence of process parameters or dye structure on intercalate properties [16,17]. Attempts have also been made to commercialise the intercalates as nano-structured pigments by combining other organo-modifiers, such as quaternary ammonium salts with long alkyl chains [18].

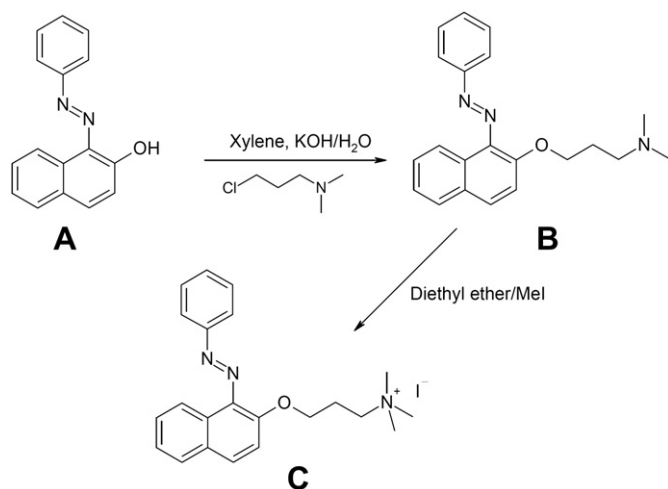
In our laboratory, we have recently used cationic dye such as rhodamine for intercalation with clay to produce dye/clay hybrid nanopigments [10], by which we improved the thermal stability of the intercalated dye. UV exposure tests on coloured polypropylene/nanopigment composites showed a significant improvement in the photo-stability compared to the polypropylene/dye samples.

Unlike cationic dyes, which can be intercalated with clay, many other commercially available dyes are non-ionic. Examples of such non-ionic dyes include azo dyes and disperse dyes. Due to their non-ionic nature these dyes cannot be intercalated with clay by ion-exchange methods. To address this problem, chemical modification methods can be adopted using the chemical synthesis route to modify these commercially available dyes into their respective cationic species. Once modified into a cationic species, these dyes can then be intercalated or adsorbed on smectite clays to produce the dye/clay hybrid nanopigments.

In this paper, the authors report the synthesis of water soluble cationic dyes using two azo dyes, namely solvent yellow 14 (SY14) and solvent red 24 (SR24), and one disperse dye, disperse red 60

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Scheme 1. Modification of the azo dye SY14.

(DR60), and their subsequent intercalation with  $\text{Na}^+$ -MMT to form nano-structured pigments or nanopigments. This paper will also present X-ray diffraction (XRD) and thermogravimetric analysis (TGA) studies performed on these nanopigments.

## 2. Experimental

### 2.1. Materials

Dyes used in this work included two azo dyes, namely, Solvent Yellow 14 (SY14, CI 12055) and Solvent Red 24 (SR24, CI 26105), and one disperse dye, Disperse Red 60 (DR60, CI 60756), which were supplied by Allied Colors and Additives, Australia. Other chemicals used were: xylene (Merck), potassium hydroxide (BDH), 3-dimethylamino-1-propylchloride hydrochloride salt, and potassium carbonate (Aldrich). Na-montmorillonite used was Cloisite  $\text{Na}^+$  from Southern Clay.

### 2.2. Molecular characterisation

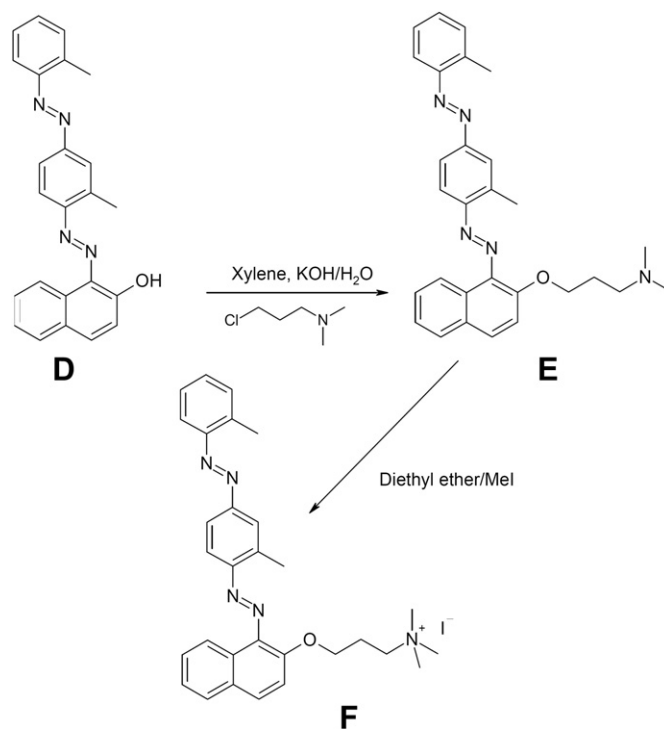
Nuclear magnetic resonance spectra were recorded on a Bruker AM-300 spectrometer operating at 300.13 MHz (1H). The electro-spray mass spectra were obtained on a Perkin–Elmer Sciex API-300 triple quadrupole mass spectrometer in positive ion mode with acetonitrile as solvent (uncertainty\_0.3).

### 2.3. Chemical modification of dyes

The phenolic groups of the azo dyes SY14 and SR24 as well as Disperse dye DR60 can be alkylated using a suitable alkylating agent, such as 3-dimethylamino-1-propylchloride hydrochloride salt. Accordingly, these dyes were converted to their corresponding tertiary amines by reacting with 3-dimethylamino-1-propylchloride hydrochloride in the presence of potassium hydroxide in xylene under refluxing condition for 48 h. Usual work-up gave the corresponding amines. These amines were then treated with methyl iodide in diethyl ether at room temperature, to give the desired salts as crystalline solids. The details of the reactions are given in the following Schemes 1, 2 and 3 respectively.

#### 2.3.1. Synthesis of trimethyl-[3-(1-phenylazo-naphthalen-2-yloxy)-propyl]-ammonium iodide (C) (Scheme 1)

20 g of 1-Phenylazo-naphthalen-2-ol (SY14, A) were stirred with 300 ml of hot xylene. A solution of 5 g of potassium hydroxide in



Scheme 2. Modification of the azo dye SR24.

20 ml of water was slowly added with stirring. The mixture was refluxed until the water was entirely removed. After cooling to about 70 °C, the free base (prepared from 16 g 3-dimethylamino-1-propylchloride hydrochloride salt with potassium carbonate and extraction with 50 ml of xylene) was added. The mixture was refluxed for 48 h, cooled to room temperature and filtered. The filtrate was distilled to dryness and the residue (B) was dissolved in 300 ml of ether and added 15 g iodomethane and stirred at RM for 48 h. The solid which separated was filtered off and washed with more ether to give the crude product. This was finally recrystallised from water to give the (20 g, 52%) pure product (C) as amino salt of SY14, mp.198–200 °C.

<sup>1</sup>HNMR (DMSO- $d_6$ ): 2.16, m, 2H,  $\text{CH}_2$ ; 3.00, s, 9H, 3 $\text{CH}_3$ ; 3.42, m, 2H, N- $\text{CH}_2$ ; 4.24, t, 2H,  $\text{OCH}_2$ ; 7.46–8.25, m 11H, ArH. ESMS:  $\text{M}^+$  = 348.3.

#### 2.3.2. Synthesis of trimethyl-[3-(1-(2-methyl-4-o-tolylazo-phenylazo)-naphthalen-2-yloxy)-propyl]-ammonium iodide (F) (Scheme 2)

20 g of 1-(2-Methyl-4-o-tolylazo-phenylazo)-naphthalen-2-ol (SR24, D) were stirred with 300 ml of hot xylene. A solution of 3.5 g of potassium hydroxide in 15 ml of water was slowly added with stirring. The mixture was refluxed until the water was entirely removed. After cooling to about 70 °C, the free base (prepared from 10 g 3-dimethylamino-1-propylchloride hydrochloride salt with potassium carbonate and extraction with 50 ml of xylene) was added. The mixture was refluxed for 48 h, cooled to room temperature and filtered. The filtrate was distilled to dryness and the residue (E) was dissolved in 300 ml of ether. 10 g iodomethane was added and stirred at RM for 48 h. The solid which separated was filtered off and washed with cold ether to give the crude product. This was finally extracted with diethyl ether using Soxhlet extraction to give the (20 g, 62%) pure product (F) as amino salt of SR24, m.p. 88–90 °C.

<sup>1</sup>HNMR (DMSO- $d_6$ ): 2.24, m, 2H,  $\text{CH}_2$ ; 2.69, 3H,  $\text{CH}_3$ ; 2.78, 3H,  $\text{CH}_3$ ; 3.00, s, 9H, 3 $\text{CH}_3$ ; 3.46, m, 2H, N- $\text{CH}_2$ ; 4.32, t, 2H,  $\text{OCH}_2$ ; 7.32–8.49, m 13H, ArH. ESMS:  $\text{M}^+$  = 480.3.

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