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Development of novel fluorescent offset ink based on coumarin dyes: Synthesis and properties

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ABSTRACT

Novel fluorescent inks based on coumarin dyes used in offset printing techniques were developed, and their considered chemical and physical properties were investigated. First, the influences of very long alkyd resin, maleic varnish, and phenolic varnish substrates and dye concentrations on the fluorescence properties of these dyes, and secondly, the effects of the presence of fluorescent dyes on the physical properties of inks were examined. Accordingly, two offset inks were prepared: one with an obtained optimum formulation possessing the strongest fluorescence emission in alkyd resin and maleic varnish with a weight ratio of 60:40, and one without fluorescent dyes. Their physical properties, such as rheological behavior, tack, and ink-in-water emulsification, were studied. Both inks showed Newtonian behavior, and the dye induced small increases in the viscosity, thixotropy, and tack values of the fluorescent ink.

1. Introduction

Coumarin derivatives are important commercial organic fluorescent materials because of their intense fluorescence and applications in the coloration of synthetic fibers [1–4]. Additionally, these dyes are widely employed as laser dyes, fluorescent brightening agents, and as organic nonlinear optical materials in industry [1–6]. Recently, they have been utilized in solar energy collectors, organic light-emitting diodes (LED), and numerous biological applications [1–3].

Daylight fluorescent colorants are widely used in special inks, and highlighting markers. The last two decades have seen remarkable growth in the field of security inks, in which fluorescent inks are of considerable interest [7–13]. In an earlier study, a fluorescent offset ink based on the inorganic pigment phosphor $BaCaBO_3F$: Eu^{3+}, Li^+ was reported [11]. To the best of our knowledge, however, there are few reports regarding this issue. Herein, an offset printing technique which uses a novel fluorescent ink based on coumarin dyes was studied because of its low casting, high quality in bulk quantities, and ease of application onto various surfaces [7].

In the continuance of our previous studies [4], three coumarin dyes possessing electron-donator groups such as the *N*,*N*-diethylamino group and electron-acceptor heterocyclic moieties such as benzimidazole, and benzoxazole with high fluorescence quantum yield and light fastness were synthesized, and their fluorescence properties were studied in various common offset printing resins. The influences of resin substrate, dye concentration, and functional groups on the solid-state fluorescence properties of these dyes were investigated by spectrofluorometry. Furthermore, the effects of the presence of fluorescent dye on the physical properties of inks were studied.

2. Experimental

2.1. Materials and methods

Chemicals for the synthesis of coumarin derivatives were purchased from Merck and used without further purification. Rheology modifier Clayton AF was purchased from (Rockwood). The very long alkyd resin chosen for formulating was obtained from Azaran Baspar Ltd., maleic and phenolic varnish and distillate petroleum oil from Iran Ink Ltd., and Ca/Co dryer from Bonyan Kala Chemie Ltd. The security paper was from Jin Hanjiang (China). The resinous films were prepared using a coater from a paint drying recorder from Mickle Laboratory Engineering Co. Ltd. Ink vehicles were mixed by laboratory mixer, Heidolph RZR 2020. Grinding of the samples was performed by automatic muller dispersion from Asia Rose fame Pardis. Printability of the inks was examined using a

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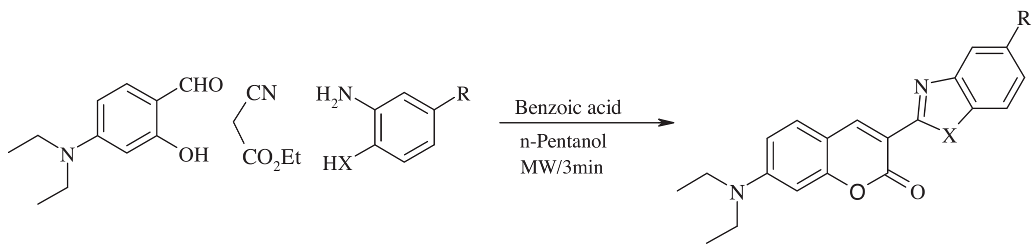

2 3 4 1(a-c)

Compound	X	R
1a	O	Cl
1b	O	CH_3
1c	N	H

Scheme 1. Synthesis of the coumarin derivatives.

Past Ink Proofer, RK. Microwave irradiation was applied using a microwave, LG MC-9283JLR.The emission spectra were obtained using a fluorescence spectrophotometer, Perkin-Elmer Ls55. Rheological properties were measured using a Rheometer Anton-Paar MCR300 with cone and plate geometry. Tack values were measured on a Tack-o-Scope SW. Water pick-up was performed using a Duke Ink-Water Emulsification Tester.

2.2. General synthetic procedure of coumarin derivatives

Three coumarin based fluorescent dyes were synthesized applying the microwave-assisted (MU) one-pot procedure according to our previous studies [4] as is shown in Scheme 1. The purity of the synthesized dyes (more than 90%) was monitored by thin layer chromatography (TLC).

2.3. Ink formulation

Offset inks with and without fluorescent dyes were prepared using a typical composition for printing ink, shown in Table 1. A thoroughly-blended mixture of very long alkyd resin, maleic varnish, solvent, and dryer was prepared in a laboratory mixer. Then, the dye (for the fluorescent ink), talc, calcium carbonate, and rheology modifier were added. Finally, a homogenous mixture was obtained which was then milled by an automatic Muller dispersion apparatus.

2.4. Fluorescent properties measurements

The emission spectra of the 37 μm resinous films were recorded in a front facing arrangement in a solid sample holder using a 1% filter. The fluorescence quantum yields of the prepared films were calculated relative to anthracence in the respective media.

Table 1
A typical formulation for fluorescent offset printing ink [14].

Constituent	Quantity (%, w/w)
Fluorescent dye	1
Very long alkyd resin[a]	54
Maleic varnish	36
Talc	3
Calcium carbonate	1
Distillated petroleum oil (boiling point 240)	2
Rheology modifier Clayton AF	2
Ca/Co dryer	1

[a] Oil content (oil length = 66).

It was assumed that the anthracence quantum yield ($\Phi_F = 0.25$) was unchanged inthe three resinous films prepared using very long alkyd resin, maleic varnish, or phenolic varnish media[15,16].The fluorescence quantum yields of dyes **1**(a–c) in solution were estimated by comparing them with 1,1,4,4-tetraphenyl-1,3-butadiene in ethanol ($\Phi_F = 0.7$), based on the reference [17].

2.5. Measurements of physical properties of inks

The physical properties of the inks, such as their rheological properties (steady shear viscosity, thixotropy, and temperature-dependent viscosity), tack, and ink-water emulsification, were studied. The steady shear viscosity was measured under shear rates ranging from 0.1 s^{-1} to 100 s^{-1} at 25 °C. In order to investigate the thixotropic behavior of the inks, the shear rate was increased linearly from 0.1 to 100 s^{-1} and then linearly reduced to 0.1 s^{-1}. The viscosity of inks was studied as a function of temperature across a range from 25 to 60 °C at a fixed shear rate of $\dot{\gamma} = 50\,s^{-1}$. Tack values were measured at different speeds and 25 °C according to the British standard ISO 12634. Water pick-up was tested according to the ASTM D4942 standard.

3. Results and discussion

3.1. Emission properties of the coumarin derivatives

3.1.1. In solution

All the dyes **1**(a–c) were excited at 435–436 nm and showed green fluorescence emission with high intensity (λ_{max} emission at 490–500 nm). Fig. 1 shows fluorescence emission spectra of 10^{-7} M acetonitrile solutions of the three dyes. The important fluorescence characteristics like quantum yield (Φ), oscillator strength (f) and Stokes shift (υ_A-υ_F) were studied for these dyes, where A = absorption and F fluorescence.

The fluorescence quantum yield (Φ_f) values were calculated using Eq. (1), and referred to 1,1,4,4-tetraphenyl-1,3-butadiene dye in ethanol ($\Phi_{ref} = 0.7$) [17],

$$\phi_{sample} = \phi_{ref}\left(\frac{F_{sample}}{F_{ref}}\right)\left(\frac{A_{ref}}{A_{sample}}\right)\left(\frac{n^2_{sample}}{n^2_{ref}}\right) \quad (1)$$

where, F_{sample}, A_{sample}, n_{sample} and F_{ref}, A_{ref}, n_{ref} are relative integrated fluorescence intensities, absorbance at excitation wavelength, and refractive index of the sample and reference, respectively.