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Synthesis of Fluoran Dyes with Improved Properties

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ABSTRACT

Three fluoran dyes having black, green and red colors respectively, were synthesized and their structures verified by IR spectra and elemental analysis. Static and dynamic color development tests and thermal analyses proved that, with the addition of ester type sensitizers, the dyes can lower the temperature and accelerate the rate of color development and increase the optical density of the developed color of thermal sensitive paper.

1 INTRODUCTION

Fluoran dyes are widely used as thermal sensitive dyes in thermal sensitive materials with an estimated (in 1989) increasing demand of 20% annually.[1] They cover the whole color spectrum including yellow, red, green and black, and are the only thermal sensitive dyes that can give a black color from a single chemical structure. Fluoran itself is colorless or only slightly colored (proton acceptor); the central carbon atom forms a bond with other atoms by sp^3 hybrid orbitals to form the colorless lactone ring. When the dye is exposed to a color developer (proton donor), the lactone ring is opened and the hybridized sp^3 orbital of the central carbon atom is converted to an sp^2 hybrid orbital. The dye molecule thereby takes the form of a coplanar continuous conjugated system, while increasing the overlapping of π electrons, with reduced molecular excitation energy causing the maximum absorbance of the molecule to shift into the visible region, i.e. showing color.

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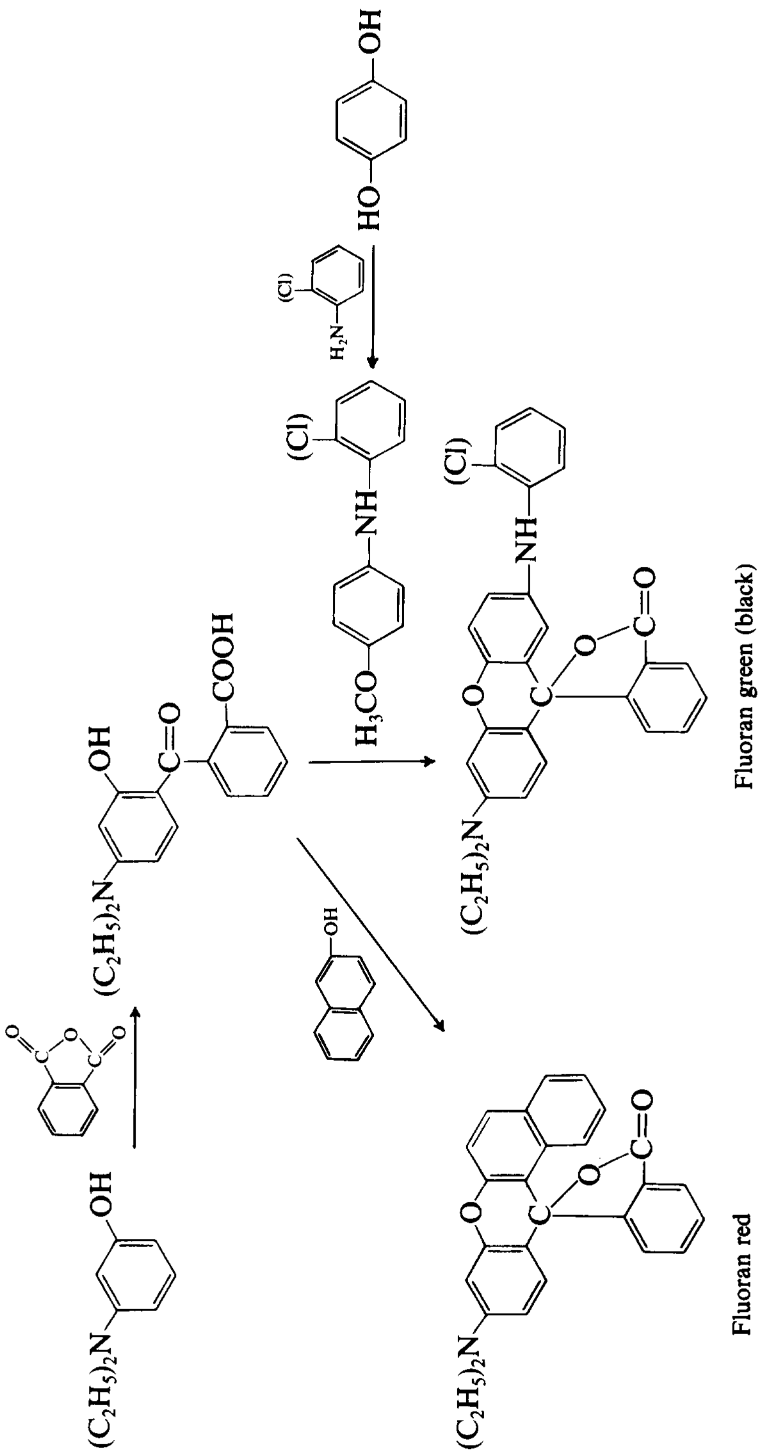


Scheme 1

The addition of cheap sensitizers to the fluoran dye system results in specific features of high sensitivity and accelerated rate of color development, higher optical density and more stable color image. The present paper describes the synthesis of three fluoran dyes having black, green and red colors (Scheme 1).

2 EXPERIMENTAL

2.1 Apparatus and chemicals

The following instrumentation was used: IR spectroscope 5DX FT-IR (Nicolet, USA), liquid chromatograph (Varian 5060, USA), elemental analyser CHN CORDER MF3 (Yanaco, Japan), thermal analyser DT-20B (Shimazu, Japan), static color developer TZH-1 (Tianjin Paper Research Institute), dynamic color developer TH-PMD (Japan), reflection densitometer MCF-1 (Guangzhou, China), spectrophotometer UV 751 (Shanghai, China).

Chemicals used were: *m*-hydroxy-*N*,*N*-diethylaniline (industrial grade), phthalic anhydride (industrial grade), aniline (c.p), *o*-chloroaniline (industrial grade), *β*-naphthol (industrial grade), hydroquinone (c.p), dimethyl sulfate (c.p), phosphoric acid (c.p), sulfuric acid (c.p), xylene (c.p) and toluene (c.p).

2.2 Synthesis of 3-dimethylamino-7-(*o*-chlorophenylamino)fluoran (fluoran black)

2.2.1 2-Hydroxy-4-diethylamino-2'-carboxylbenzophenone (intermediate A)
m-Hydroxy-*N*, *N*-diethylaniline (16·5 g, 0·1 mol) and phthalic anhydride (15·0 g, 0·102 mol) in xylene (60 ml) were refluxed for 5 h. After removal of the xylene, a pink colored material was obtained.

2.2.2 4-Methoxy-2'-chlorodiphenylamine (intermediate B)
o-Chloroaniline (10·8 ml, 0·1 mol), hydroquinone (11·6 g, 0·105 mol) and 85% phosphoric acid (4·5 ml, 0·066 mol) in *o*-dichlorobenzene (50 ml) were reacted at 175 + 2°C for 6 h. After removing *o*-dichlorobenzene, 20 ml 20% aq. sodium hydroxide and 10·4 ml (0·110 mol) of dimethyl sulfate were added to the residue oily layer and the mixture heated at 70°C for 2 h; after filtering and drying, a light brown colored solid was obtained.

*2.3.3 3-Diethylamino-7-(*o*-chlorophenylamino)fluoran*
2-Hydroxy-4-diethylamino-2'-carboxylbenzophenone (9·4 g, 0·03 mol), 4-methoxy-2'-chlorodiphenylamine (7·1 g, 0·029 mol) and 98% sulfuric acid

(29 ml, 1·78 mol) were reacted at 20–25°C for 24 h. The reaction mixture was poured into ice water, filtered and the product washed neutral. The filter cake thus obtained was then refluxed with 20% aq. sodium hydroxide (30 ml) and 25 ml toluene for 2 h; the product was filtered and recrystallized from toluene to give an off-white solid.

2.3 3-Diethylamino-7-phenylaminofluoran (fluoran green)

Using the same procedure as in section 2.2, but using aniline instead of *o*-chloroaniline, intermediate C and 3-diethylamino-7-phenylaminofluoran were obtained, which after recrystallization from ethanol gave a white solid.

2.4 3-Diethylamino-7, 88-benzofluoran (fluoran red)

To a mixture of 2-hydroxy-4-diethylamino-2'-carboxylbenzophenone (10·4 g, 0·033 mol) and β-naphthol (4·3 g, 0·03 mol) was added 98% sulfuric acid (29 ml, 1·78 mol) and the mixture reacted at 20–25°C for 24 h. The reaction mixture was poured into ice water, the product filtered and washed neutral. The filter cake was stirred into 1% aq. sodium hydroxide (100 ml) at 75–80°C for 4 h, the liquor filtered while hot and the product recrystallized from 95% ethanol, to obtain a light red solid.

3 RESULTS AND DISCUSSION

3.1 Synthesis and electronic spectra data of the fluoran dyes

Yields and characterization data for the three black, green and red fluoran dyes are shown in Tables 1 and 2. The structures were verified by IR and elemental analysis. Absorption spectra data for the dyes are shown in Fig. 1. With the black and green dyes, there are two absorption bands (x and y bands) in the longer and lower visible region respectively. The green dye shows absorption at λ_{max} 610 nm (giving a blue color) and at λ_{max} 440 nm (giving a yellow color), thus producing a visually perceived green color. In the black dye, a chlorine substituent is present in the *ortho* position of the aniline moiety, resulting in steric hindrance which prevents the aniline moiety maintaining a planar configuration with respect to the fluoran nucleus. Electron interaction between the aniline moiety and the fluoran nucleus is thus inhibited, resulting in a hypochromic shift of the x band to 585 nm (giving a violet color); the chloro substitution has little effect on the y band. This dye, therefore, has a visually perceived additive effect of violet and yellow, resulting in a black dye.

TABLE 1
Physical Properties, Elemental Analysis and IR Data for Intermediates

Intermediates	Yield (%)	Purity (%)	M.p. (°C)	Analysis (% calc.) C	H	N	Cl	IR (cm^{-1})
A	86·4	98·6	206–208	68·98 (69·00),	6·18 (6·11),	3·99 (4·47)		3427·0 (—OH), 1691·7 (C=O), 1344·5 (C—N), 1197·9 (C—O)
B	85·3	90·0	62–63	67·14 (66·81),	5·23 (5·18),	6·43 (6·00),	15·11 (15·17)	3402·3 (—NH), 1317·5 (C—N), 1049·3 (C—O—C)
C	83·2	96·3	104–105	78·40 (78·36),	6·70 (6·58),	7·03 (7·05)		3373·5 (—NH), 1332·0 (C—N), 1029·4 (C—O—C)

TABLE 2
Physical Properties, Elemental Analysis, IR and λ_{max} Data for Fluoran Dyes

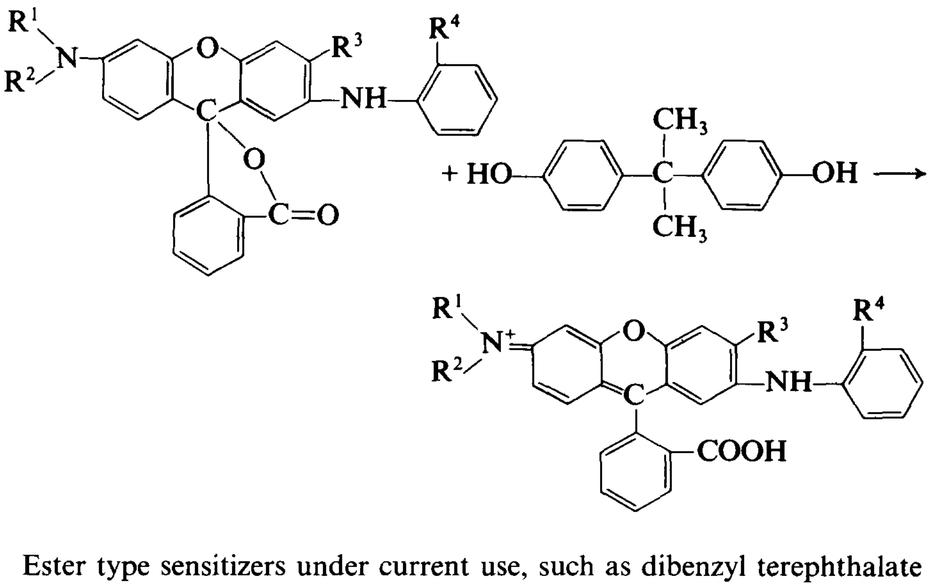
Fluorans	Yield (%)	Purity (%)	M.p. (°C)	Analysis (% calc.) C	H	N	Cl	IR (cm^{-1}) —NH	C=O	C—N	Ø—O—Ø	λ_{max} (nm) (95% C_2H_5OH—HCl)	
Black	75·2	97·6	223–226	72·77 (72·50),	5·14 (5·07),	5·39 (5·64),	7·13 (7·13)	3361·3	1753·5	1329·0	1236·5	435	585
Green	71·1	93·0	202–204	78·19 (77·92),	5·99 (6·06),	6·22 (5·63)		3353·0	1733·7	1321·6	1234·7	440	610
Red	70·6	94·2	215–217	79·72 (79·82),	5·74 (5·46),	3·22 (3·33)			1761·1	1346·4	1236·5	528	

3.2 Improved properties of the synthesized fluoran dyes

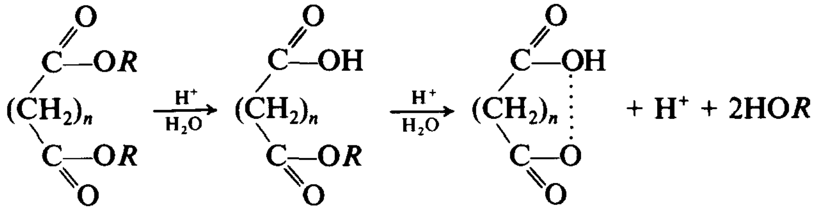
3.2.1 Improved sensitivity for color development

Fluoran dyes are the main color forming components of thermal sensitive materials. Research and development of potentially ideal fluoran dyes is particularly concerned with properties such as low melting points, high sensitivity and good image stability. Fluoran dyes having such properties usually require complicated and lengthy synthetic procedures and are therefore relatively expensive. Fluoran dyes generally have m.p. above 160°C, and their eutectic points, when mixed with a developer, are still too high to meet the requirement for high sensitivity recording. The three fluoran dyes synthesized in this present report, despite their high melting points of over 200°C, have the advantage of an easier synthetic approach, and they possess good light and heat resistant properties, with satisfactory whiteness, as well as high sensitivity and optical density. For further improvement in their sensitivities, the addition of cheap sensitizers could be of value, for use in modern high speed facsimile communication.

The rapid color forming reaction between the fluoran dye and the color developer under the influence of sensitizers in highly sensitive thermal sensitive paper is as follows.[2]



Ester type sensitizers under current use, such as dibenzyl terephthalate (DBT) and dibenzyl isophthalate (DBI) are hydrolyzed when the thermal sensitive papers are exposed to heat, releasing protons which accelerate the color development.[3]



Static and dynamic color development tests were carried out on thermal sensitive papers coated with fluoran black and bisphenol A with addition of DBT and DBI. The results are shown in Figs 2 and 3.

After the addition of sensitizers, the temperature for color development was lowered and, the optical density increased, thus giving characteristics of accelerated color development and high sensitivity.

Because ester type sensitizers release H^+ during color development, to accelerate color development, the acidity of the free acid generated on hydrolysis can influence the sensitivity of fluoran dye color development. When fluoran black was incorporated separately with DBT and DBI, the acids produced on hydrolysis were terephthalic acid (pK_{a_1} = 3·82) and isopthalic acid (pK_{a_1} = 3·28), respectively; isophthalic acid is the stronger acid, while DBI has the lower melting point of 83–84°C and therefore, it exhibits a better sensitizing effect.

Thermal sensitive materials generally develop colors during the melting of the fluoran dyes and the developer. The melting temperatures of fluoran dyes and bisphenol A (m.p. 156°C) were rather high, therefore requiring a higher color developing temperature with concomitant lower sensitivity.

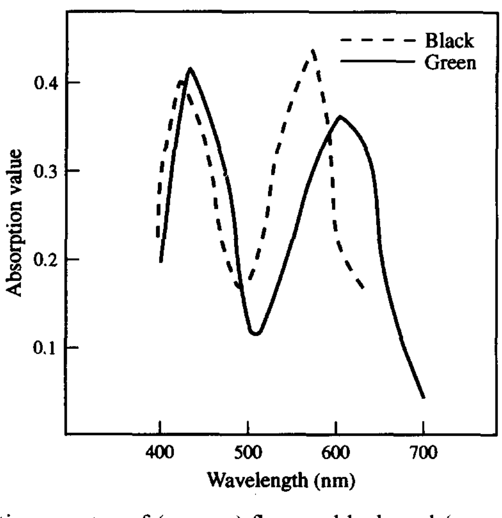


Fig. 1. Absorption spectra of (– – – –) fluoran black and (———) fluoran green.

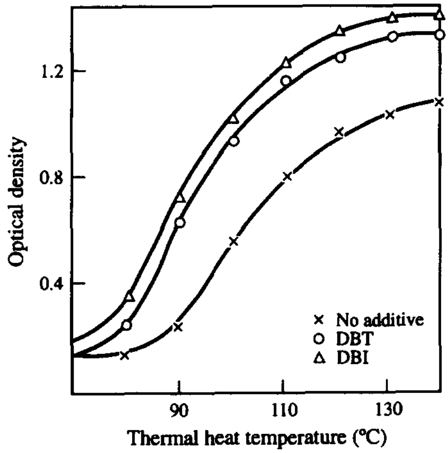


Fig. 2. Static image densities: ×, no additive; ○, DBT; Δ, DBI.

The black, green and red fluoran dyes synthesized in this report, when mixed with bisphenol A in a 1:3 ratio, showed, on thermal analysis studies, that all the binary eutectic points fell above 110°C. Sensitizers generally have lower melting points (DBT, m.p. 95–96°C; DBI, m.p. 83–84°C). Viscosities and heat of fusion at their respective melting range were comparatively low. They are easily compatible with fluoran dyes and bisphenol A, and act as agents to lower the melting point of mixtures of fluoran dyes and bisphenol A. Thermal analysis curves were smooth and sharp (Fig. 4). The tricomponent eutectic points of the three fluoran dyes with sensitizers are given in Table 3. Generally, the optimum eutectic point of thermal sensitive paper falls in the range 60–75°C.

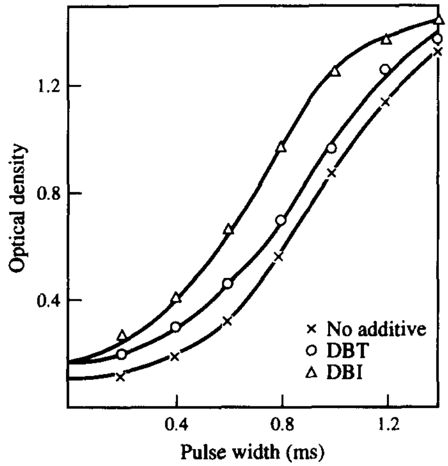


Fig. 3. Dynamic image densities: ×, no additive; ○, DBT; Δ, DBI.

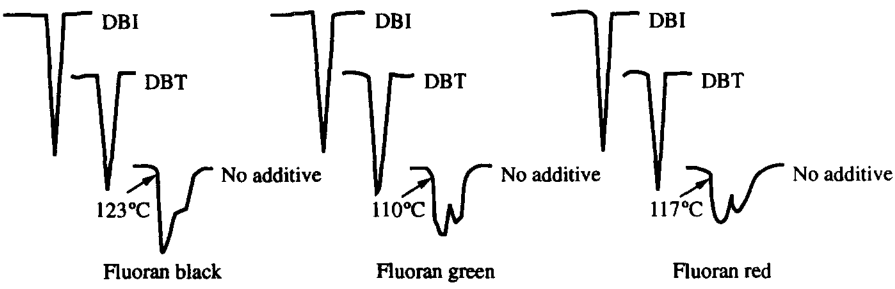


Fig. 4. DSC curves of fluorans/bisphenol A/sensitizers (1/3/2).

TABLE 3
Eutectic Point of Fluoran/Bisphenol A/Sensitizer Systems (1/3/2)

Fluorans	*Sensitizers*	*Eutectic point (°C)*
Black	DBI	68
	DBT	75
	No	123
Green	DBI	62
	DBT	69
	No	110
Red	DBI	64
	DBT	71
	No	113

While a high eutectic point causes lower color developing sensitivity, too low a eutectic point may affect the whiteness of the thermal paper.

3.2.2 Stability properties

Fluoran black in thermal sensitive paper exhibits good light fastness and heat stability characteristics, but is less anti-ageing and has lower fastness to plasticizers (Table 4).

The addition of sensitizers can also help to increase image stability, because fluoran dyes have an acidic color developing mechanism. The opening of the lactone ring is a reversible reaction:

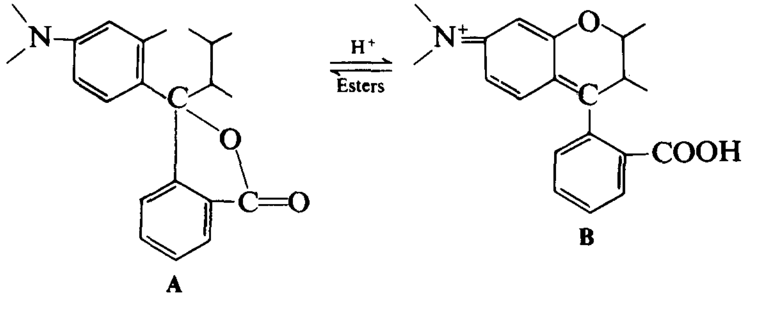


TABLE 4
Fastness Properties of Fluoran Black

Fastness	*Process*	*Optical density before test*		*Optical density after test*	
		D_0	D	D_0	D
Light	Fluorescent lamp 5000 lux, 70 h	0·08	1·43	0·11	1·38
Heat	50°C, 24 h	0·08	1·41	0·10	1·36
Ageing	40°C, RH 90%, 24 h	0·08	1·41	0·10	1·12
Plasticizer	50°C, 24 h, 20 g cm^{-2}	0·08	1·38	0·08	0·95

The forward reaction results in the formation of the colored xanthene compound **B**. However, in the presence of plasticizers or fatty compounds, the reaction proceeds in the reverse direction with the formation of the original colorless fluoran dye **A** with concomitant decrease of image stability. In order to increase the stability, in addition to efforts to find new types of fluoran dyes, it is also possible to add sensitizers which can liberate H^+, thus causing the reaction to proceed in the forward direction, while hindering the reverse color fading reaction. Stability tests were carried out by the addition of DBT and DBI into a fluoran black and bisphenol **A** system; when subjected to a temperature of 40°C and a relative humidity of 50% for 24 h, dynamic color development curves were obtained (Fig. 5). The test showed that the change in color intensity was very slight, suggesting that the sensitizers can increase the stability of the image.

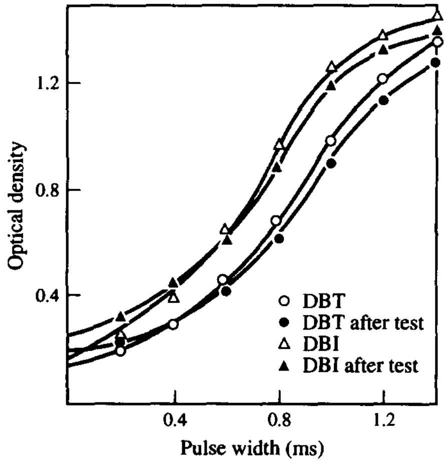


Fig. 5. Imaging stabilization of sensitizers DBI and DBT.

4 CONCLUSIONS

Fluoran dyes with a black, green and red color were synthesized in good yield and purity. With the addition of sensitizers, a fluoran dye and bisphenol **A** system required a lower temperature, and resulted in an accelerated rate of color development, while increasing the optical density at the same time. The structures also had beneficial effects on the stability of the developed image.

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