Dyes and Pigments **23** (1993) 33–42

New Heat-Sensitive Irreversible Colour Former Derived from Aromatic Isocyanates and Imino Compounds

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(Received 2 March 1993; accepted 7 April 1993)

ABSTRACT

New heat-sensitive irreversible colour former systems were first developed by the reaction of aromatic isocyanates with imino compounds. This colour developing reaction is irreversible to give pigment type chromophores, and then provides an excellent colour image with good chemical and light stabilities. The colour images can be controlled from yellow to brownish black by changing combinations of each component.

1 INTRODUCTION

Non-impact heat-sensitive recording by using leuco dyes as colour former is currently used widely as a conventional recording system. The main

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Dyes and Pigments 0143-7208/93/$06.00

technology is attained by the reaction of leuco dyes with acids to produce cationic dyes by means of heat energy from the thermal head as an information transmission means. The main problem is the reversibility of their colour developing reactions, and as a result the printed colour images are decolourized and disappear by light or in hydrophobic conditions. Many practical applications to prevent this reversible reaction are currently conducted by adding many types of stabilizers.[1] In addition, the cationic dyes produced generally have poor resistivity against light and atmospheric oxygen. These disadvantages of the leuco dye type colour former system restrict its use for applications in which the recorded images need to be kept safely for a long period.

Reversibility of the colour forming reaction can be modified chemically by using the new irreversible reactions such as the condensation or addition reactions to produce colour images. Each component is colourless at the beginning but immediately produces colour after the condensation or addition reactions. The recorded information should have good contrast on substrates, and then a black or deep brown colour image is expected.

The authors have recently developed a new heat-sensitive irreversible colour forming system by the addition reaction of the aromatic isocyanates with the imino compounds. The colour images produced were very stable to light and heat, and this colour forming system has already been commercialized.[2]

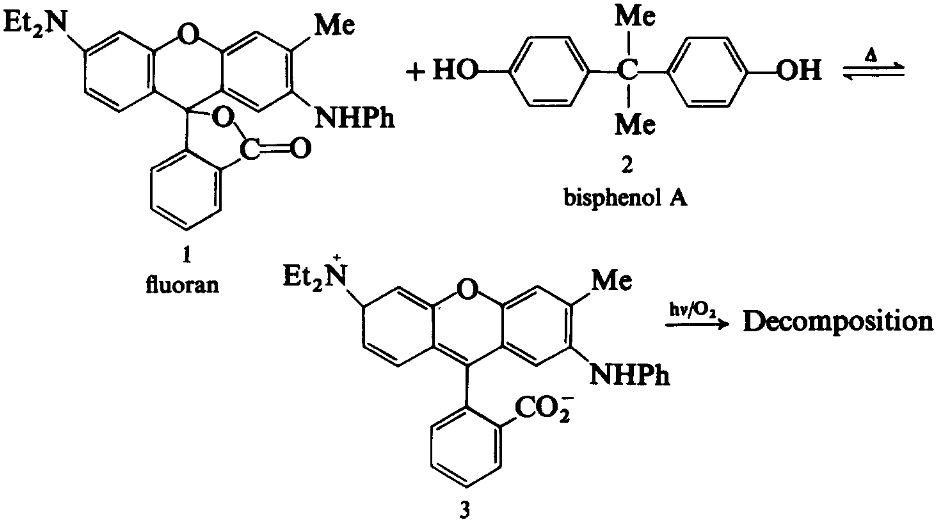
2 RESULTS AND DISCUSSION

2.1 Irreversible reaction and chromophoric system

The traditional colour forming reaction of fluoran is presented in Scheme 1. In the reaction, the cationic dye **3** is produced by the reaction of fluoran **1** with acid **2** as a developer, but the colour of **3** disappears by the reversible reaction in hydrophobic conditions to give **1** or by further photodegradation.

The printed images need to be kept for a long period, especially in the following applications: money-related receipts, scientific recording data, facsimile recording data, and so on. Irreversibility of the colour forming reaction is very important in such fields and the development of new reactions of different colour forming systems have been anticipated. The authors' new heat-sensitive irreversible colour forming system is one of the candidates which is shown in Scheme 2.

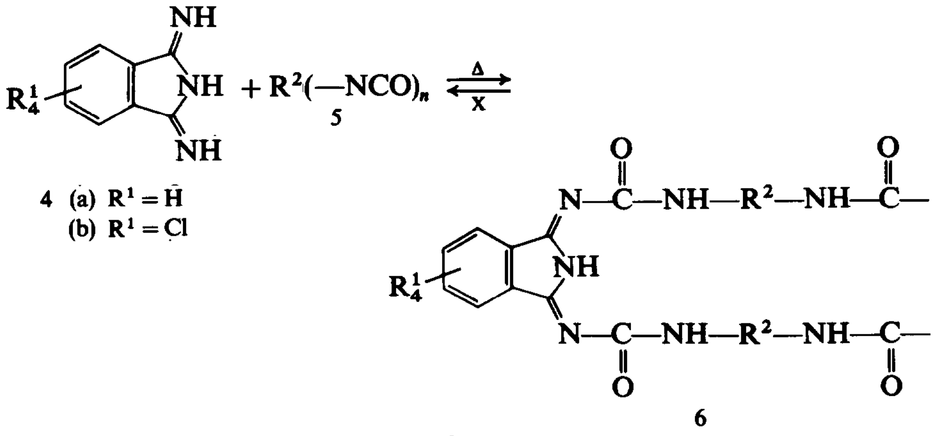
The addition of imine **4** to isocyanate **5** gave the isoindolenine type pigments **6** which have various colours depending on the combinations of



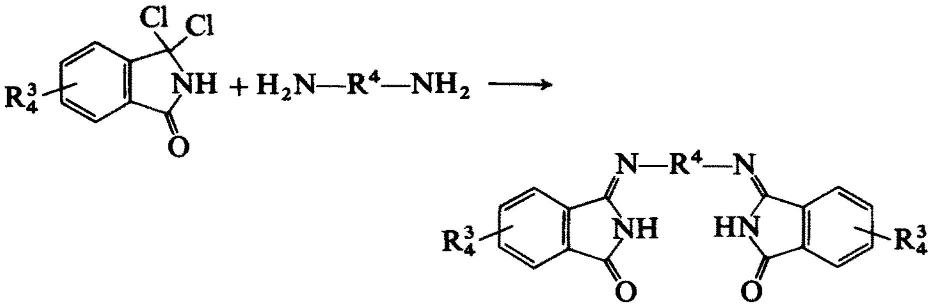
Scheme 1

each component **4** and **5**. The basic chromiophoric system of the product **6** is well known in pigment chemistry. The pigments were synthesized by the reaction of 3,3-dichloro-4,5,6,7-tetrahalogenophthalimides with various diamines, as shown in Scheme 3. It is well known that the pigments have been commercialized and have excellent chemical stabilities, and resistance to light and heat.[3]

The Pariser Parr Pople Molecular Orbital (PPP MO) calculation method revealed that dye **6** has weak intramolecular charge-transfer chromophoric systems and that the carbamoyl moiety acts as a donor and the imide moiety acts as an acceptor. In the solid state, the reaction of **4** with **5** is initiated by



Scheme 2



Scheme 3

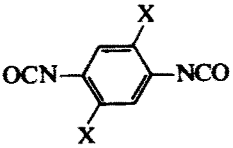
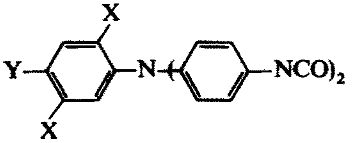
the melt of **5**; the melting point of **5** is an important factor for the performance of this colour forming system. The most useful melting point of **5** ranges from 100 to 150°C, as shown in Table 1.

2.2 Reaction of 4b with 5g in solution

The addition reaction of **4b** with **5g** was monitored in chloroform solution. The reaction proceeds step by step and many coloured intermediates were detected by GPC. After 24 h, the absorbance at 500 nm attained maximum value and the colour of the solution turned into purplish red. The time dependencies of intermediates by GPC are shown in Fig. 1.

The raw material **4b** was consumed slowly with the reaction time. The transient species A_1 ($Rt = 7{\cdot}6$ min) was produced quickly but decreased

TABLE 1
Structures and Melting Points of Isocyanate 5

No.	*n*	*Structure*			*M.p. (°C)*
a	2		X = H		95
b	2		X = OMe		180
c	2		X = OEt		133
d	2	1,5-$(NCO)_2$-$C_{10}H_6$			130
e	2		X = OMe,	Y = H	94
f	3		X = H,	Y = NCO	150
g	3		X = OMe,	Y = NCO	115
h	2	*N*-Et-3,6-$(NCO)_2$ carbazole			121

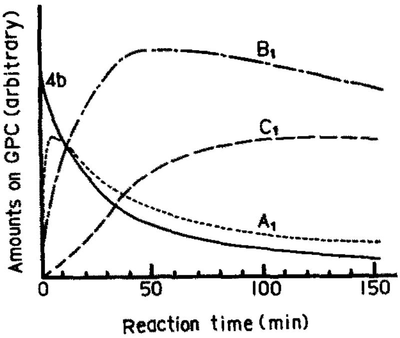
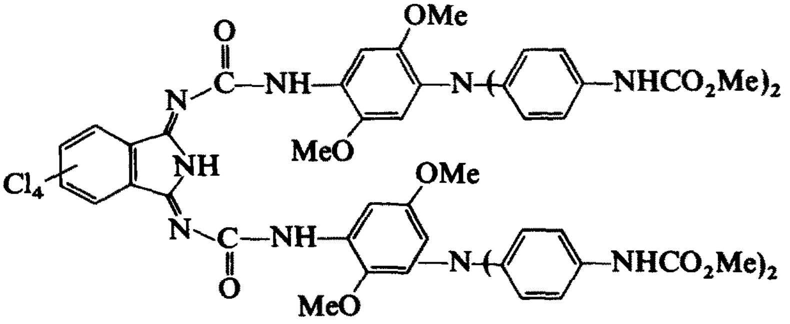


Fig. 1. Time dependence of components on GPC. *Rt*: $A = 7{\cdot}6$ min, $B = 6{\cdot}9$ min, $C = 6{\cdot}5$ min.

gradually depending on the reaction time, and products B_1 ($Rt = 6{\cdot}9$ min) and C_1 ($Rt = 6{\cdot}5$ min) were produced gradually. The colour of the reaction mixture changed from colourless at the beginning, through yellow and red, finally to purplish red.

The identification of each product was difficult because of their polymerized structures. The intermediates were isolated by adding methanol to the reaction mixture. Unreacted isocyanato groups were completely reacted with methanol to give purplish black products. These were separated by GPC and identified by FD-MS spectra. The transient species A_2 obtained from A_1 with methanol has a molecular weight of 1265 (m/z) with the chemical structure of **7** and which was obtained by the addition reaction of 2 mol of **5g** with 1 mol of **4b**. Species B_2 obtained from B_1 with methanol has a molecular weight of 2011 (m/z) which corresponds to the addition product of 3 mol of **5g** and 2 mol of **4b**. The species B_2 was produced by further reaction of A_1 with **4b** and **5g**. The absorption spectra of A_2 and B_2 in chloroform are shown in Fig. 2. Species B_2 absorbs light at much longer wavelength than A_2. Species C_2, obtained from C_1 with methanol, could not be identified because thermal decomposition of C_2 occurred during mass



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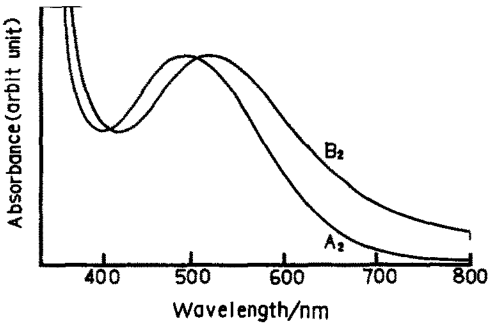

Fig. 2. Absorption spectra of components in chloroform.

spectra measurement. Species C_2 has a higher molecular weight than B_2 and might be obtained by further reaction of B_2 with **4b** and/or **5g**. From these observations, it is proposed that complicated addition reactions between **4b** and **5g** occur in solution and their product mixtures produce a brownish black colour. In the solid state, the addition reactions of **4** with **5** are proposed to be much more complex compared with those in solution. The appearance of the coloured image on the substrate (curve II) was brownish black and was compared with that of the conventional fluoran type colour former (curve I) in Fig. 3. A similar reflectance curve was obtained up to 640 nm, but fluoran (curve I) had much higher reflectance than that of the authors' (curve II) over 640 nm, and then curve II did not show real black but brownish black in colour on the substrate. The appearances of reaction products in solution between **4** and **5** are shown in Table 2. They range from yellow to brownish black in colour, depending on the combination of **4** and **5**.

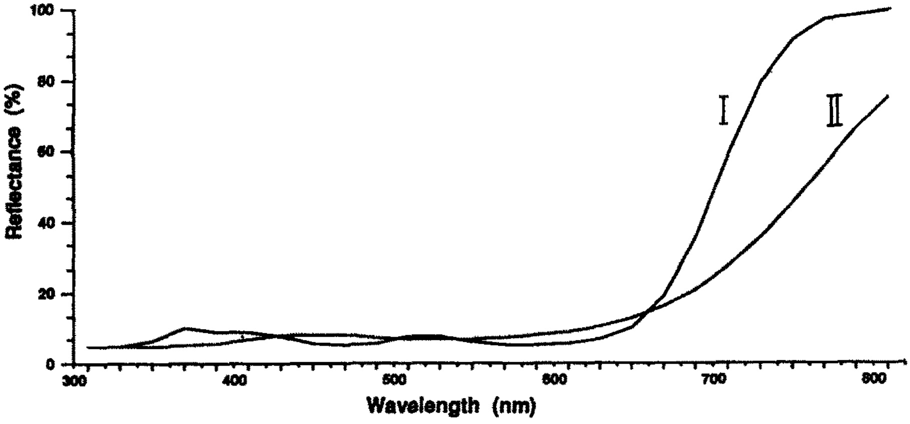

Fig. 3. Comparison of reflectance curves between I and II on coloured paper.

TABLE 2
Colour of Product from **4** and **5** in Dichlorobenzene

4	*5*	*Colour*
a	**a**	Orange
a	**b**	Brown
b	**a**	Brown
b	**b**	Brownish black
b	**c**	Brownish black
b	**d**	Brown
b	**e**	Brownish blzck
b	**f**	Brownish black
b	**g**	Brownish black
b	**h**	Brownish black

2.3 Preparation of the recording paper and their performance

The imine **4** and zinc stearate were codispersed in aqueous poly(vinyl alcohol) (PVA) solution. The isocyanate **5** and ethanol were dispersed in PVA. Additives such as antifoggant, colour developing sensitizer and calcium carbonate were mixed, and all mixtures with PVA and water were dispersed in a ball mill. Sufficient stirring was conducted to obtain a coating liquid which was coated on the base paper. This was dried and then treated by supercalendar to obtain a heat-sensitive recording paper.

TABLE 3
Comparison of Performance and Stability of Heat-Sensitive Paper Under Various Conditions

Subject	*Condition*	*I*[a]	*II*[a]
Developing system	—	Reversible	Irreversible
Developing sensitivity	—	Fast	Slow
Chromophore	—	Cationic dye	Pigment
Appearance (colour)	—	Real black	Brownish black
Stability of coloured form	—	Less stable	Stable
Coated with salad oil	40°C × 24 h	7[b]	100[b]
Dipped in water	25°C × 24 h	15[b]	99[b]
Dipped in ethanol	25°C × 24 h	4[b]	92[b]
Coated with machine oil	20°C × 60 days	83[b]	100[b]
Coated with castor oil	20°C × 60 days	5[b]	100[b]

[a] I, Commercialized fluoran type paper; II, paper of present authors.

[b] Residual optical density (ROD) $= \frac{\text{OD after test}}{\text{OD before test}} \times 100.$

The performance of the recording paper was evaluated as follows. The stabilities on storage of the authors' recording paper (II) were evaluated compared with those of a conventional commercialized recording paper (I), and the results are summarized in Table 3. Paper II has superior performances compared with I in many test subjects without slower colour developing speed. It was concluded that II has good stability on storage. The

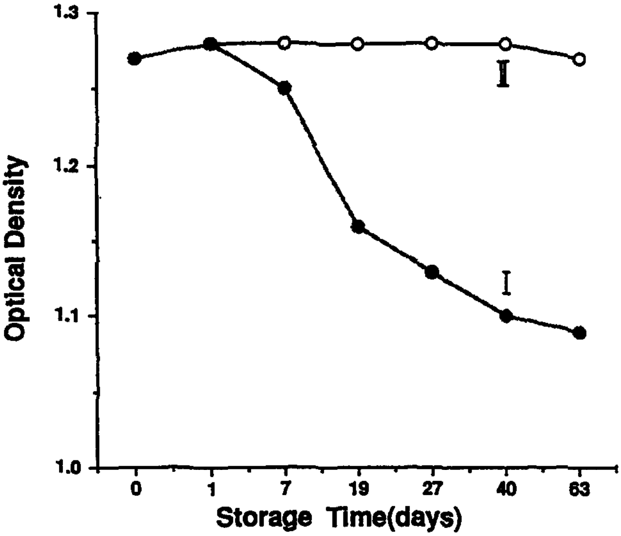

Fig. 4a. Heat and humidity stability of printed images at 40°C in 90% humidity.

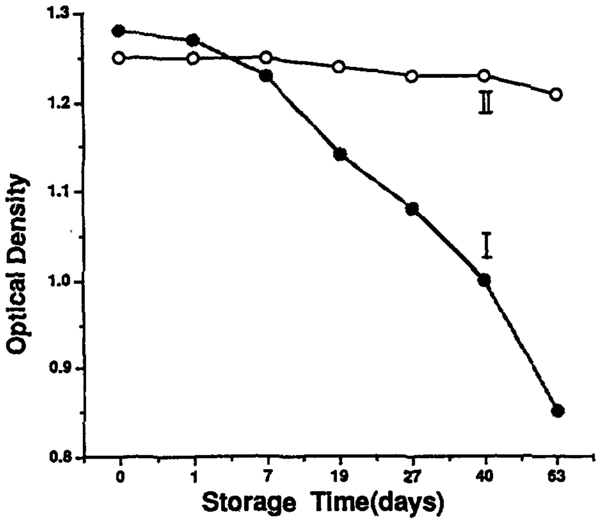

Fig. 4b. Heat stability of printed images at 60°C.

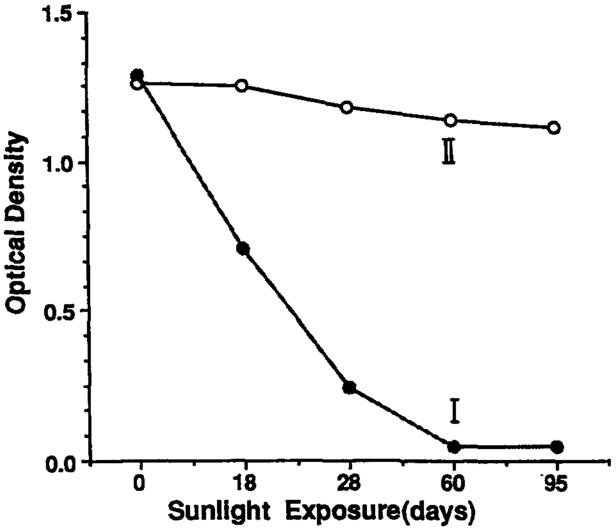

Fig. 4c. Light stability of printed images under sunlight.

stabilities of II for heat, humidity and light are shown in Figs 4a–4c compared with those of I. Paper II has superior stabilities compared with I in each condition; these are caused by irreversibility of the colour forming reaction and the stability of coloured species. In the case of paper II, the polymerized pigments typified by the chromophoric system of 7, have superior stability to heat and light.

3 EXPERIMENTS

The visible spectra were recorded on a Hitachi UV-330 spectrophotometer at 25°C. FD-MS spectra were recorded on a JEOL JMS-HX110 spectrometer. The samples for FD-MS were obtained by the reaction of **4b** with **5g** in chloroform at 25°C for 3 h, followed by methanolysis at 40°C for 1 h. The products were separated by GPC (Nippon Analytical Ind., LC-09, column: Jaigel 2H-1H, chloroform as a carrier) and each of components A_2, B_2 and C_2 was measured by FD-MS.

The imino compounds **4** were synthesized by the method reported in the literature.[4] In the case of **4b**, tetrachlorophthalic anhydride was treated with urea in chlorobenzene at 130°C for 20 h to give the imide. The imide was further reacted with phosphorus pentachloride in chlorobenzene at 130°C for 20 h and then reacted with 25% aqueous ammonia at 0°C to give **4b**.

The isocyanate **5g** was synthesized by the following method. 4-Nitro-2,5-dimethoxyaniline was reacted with 4-nitrochlorobenzene in the presence of potassium carbonate in DMF at 130°C for 60 h to give 4,4′,4″-trinitro-2,5-dimethoxytriphenylamine (m.p. 175·5–179°C). The nitro group was reduced by sodium sulphide in methanol to give the corresponding amine (m.p. 197·5–199·5°C). The amine was reacted with phosgene in toluene to give **5g**.

Syntheses of **4** and **5** were conducted at the Asahi Chemical Company and are commercially available raw materials. All other additives and materials are available as reagents.

3.1 Preparation of the recording paper.

(I) 3-Di *n* butylamino-6-methyl-7-anilinofluoran (20 g) was dispersed in 3% aqueous PVA solution (30 g). Bisphenol A (50 g) and 2-benzyloxynaphthalene (50 g) were codispersed in 3% aqueous PVA solution (150 g). The mixture of each solution was previously dispersed in a ball mill for 24 h. A dispersion of zinc stearate (10 g) in water (15 g) was added to the mixture, and calcium carbonate (50 g) in a mixture of water (80 g) and a 10% aqueous PVA solution (210 g), and then water (340 g), were added. Sufficient stirring was conducted to obtain a coating liquid which was coated on the base paper in amounts of 60 g/m^2. It was dried to the weight of 7·5 g/m^2 and then treated by supercalender to obtain a heat-sensitive recording paper (I).

(II) 1,3-Diimino-4,5,6,7-tetrachlorosoindoline (**4b**, 15 g) and zinc stearate (15 g) were codispersed in 1% aqueous PVA solution (70 g). 4,4′,4″-Triisocyanato-2,5-dimethoxytriphenylamine (**5g**, 10 g) and ethanol (7·5 ml) were dispersed in 1% aqueous PVA solution (40 g). 2-Methoxy-5-*N*,*N*-diethylsulphamoylaniline (20 g) as an antifoggant was dispersed in 1% aqueous PVA solution (80 g). 2-Benzyloxynaphthalene (20 g) as a colour developing sensitizer was dispersed in 1% aqueous PVA solution (80 g). The mixture of each solution was previously dispersed in a ball mill for 24 h. A dispersion of calcium carbonate (60 g) in water (90 ml) was added to the mixture of these four components, and then a 10% aqueous PVA solution (240 g) and water (55 g) were added. Sufficient stirring was conducted to obtain a coating liquid, which was then coated on to the base paper in amounts of 60 g/m^2. It was dried to a weight of 7·5 g/m^2 and then treated by supercalendar to obtain the heat sensitive recording paper (II).

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