

A Tamper-evident Ink

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Abstract

Ink on checks used for payment contains a reactive substance that thwarts chemical tampering. This is known as isochromatic pair ink, and contains two or more ink types that appear isochromatic despite their different dye/pigment compositions thanks to careful selection of colorants in precise amounts. They appear identical until tampered, at which point they change color due to dye dissolving. In the work reported here, an isochromatic polymerizable dye and a non-polymerizable dye were used to address issues associated with isochromatic pair ink, such as the high level of expertise required for its manufacture and deterioration of isochromatic property due to dye decomposition. The two dyes were synthesized. The print matter produced with a pair ink made using them showed good isochromatic and tamper-evident properties. The polymerizable dye dissolved less than non-polymerizable dye did thanks to stability stemming from copolymerization with the UV varnish using its polymerizable unit, while non-polymerizable dye did not have such stability.

Introduction

Fraud today often involves counterfeiting using desktop publishing programs, scanners and laser printers as well as photocopying of genuine checks. Other techniques include the use of solvents, dissolving agents and other chemicals to change check values and signatures for criminal benefit (known as chemical tampering or chemical alteration). To combat such approaches, ink containing a chemically reactive substance can be used for ground pattern printing with check values and other information. The ink undergoes color changes upon contact with the chemicals used for fraudulent activity. This noticeable effect prevents criminal tampering of checks and facilitates identification of tampered checks without the need for training or special detection devices. One type of tamper-evident ink contains certain dyes and pigments based on the difference between the high

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solubility of the former and the low solubility of the latter (Figure 1). Only the dyes dissolve in solvents and the pigments remain, creating a color change.

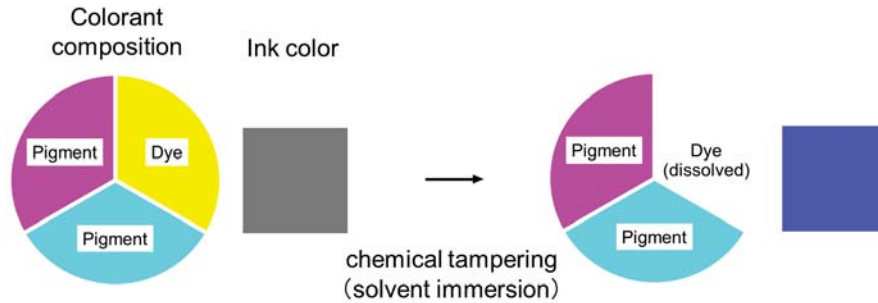


Figure 1: SEQ Figure *ARABIC 1: Tamper-evident ink.

Isochromatic pair ink is an example of the genre. The two (or more) inks used in this application have different dye/pigment compositions but appear isochromatic thanks to careful selection of colorants and their amounts (Figure 2). They appear identical without tampering, but tampering will produce color changes that create a new image such as “Void” on the check (Figure 3).

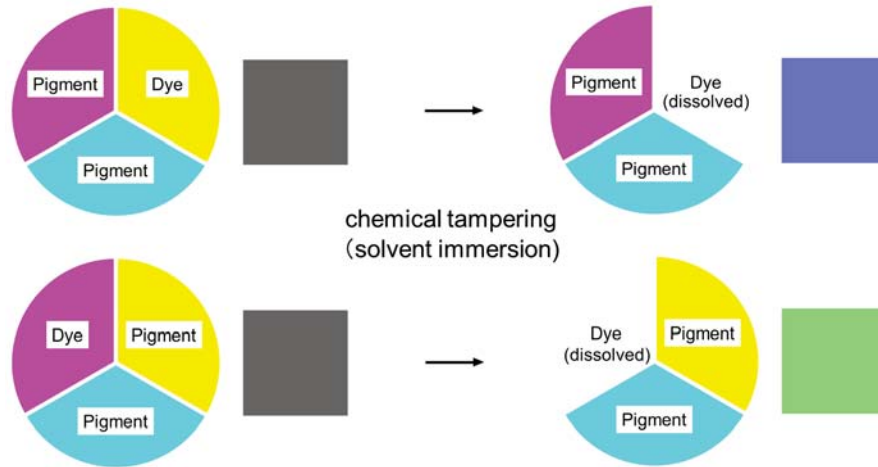


Figure 2: Isochromatic tamper-evident pair ink.



Figure 3: An application of isochromatic tamper-evident pair ink.

The development of this technique involves two problems. First, a high level of expertise is needed to establish appropriate composition for pair isochromatic inks. The spectrophotomeric curves of commercially available dyes and pigments do not generally correspond, making the development of such inks problematic. Second, different isochromatic regions also develop different appearances over time because the light-fastness of dyes is lower than that of pigments. As a result, security images designed to appear when chemical tampering is attempted may in fact appear without tampering.

Our new isochromatic tamper-evident pair ink, which consists of an isochromatic polymerizable dye and a non-polymerizable dye, is designed to overcome these challenges. The former has a polymerizable functional group (e.g., acryloyl, metacryloyl) (Figure 4) [1].

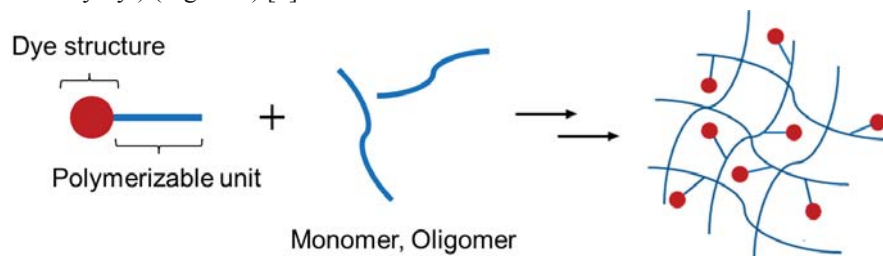


Figure 4: Polymerizable dye.

This group enables the dye to copolymerize with other polymerizable compounds such as monomers and oligomers, giving the dye high stability in the polymer structure thus formed. Certain polymerizable dyes are commercially available. In this study, the polymerizable dye 3a and the non-polymerizable dye 3b were considered (Figure 5).

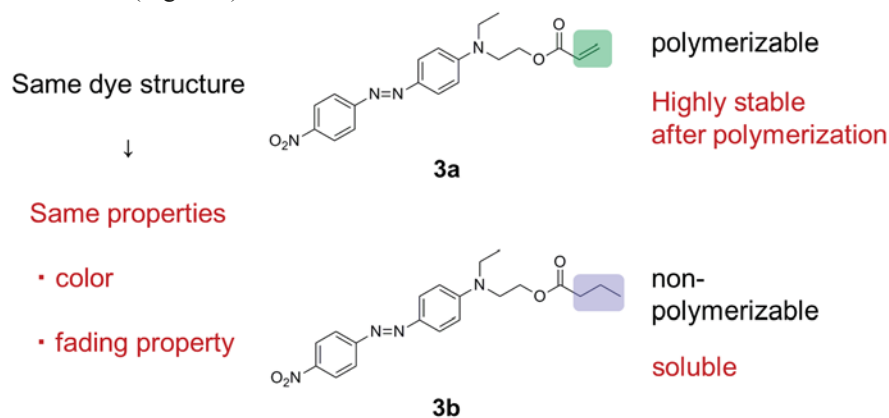


Figure 5: Core idea of this research.

As both have the same chemical structure around their azo chromophores, the dyes were expected to exhibit similar properties in considerations such as color and fading. When **3a** is used in UV ink, its acryloyl group enables the dye to bond covalently with polymer structures under UV irradiation, making it resistant to solvents. Conversely, **3b** does not develop such solvent resistance under UV irradiation and maintains high solubility. This difference in behavior under UV irradiation was leveraged to develop tamper-evident pair ink. In this research, **3a** and **3b** were first synthesized. Next, material printed with tamper-evident pair ink was examined via color evaluation.

Experimental procedure

Materials

C. I. Disperse Red 1 (dye content 95%) was purchased from the Sigma-Aldrich Chemical Company. Acrylic acid, butyric acid and N, N'-dicyclohexylcarbodiimide (DCC) were obtained from Wako Pure Chemical Industries. Tetramethylsilane (TMS), 4-(dimethylamino)pyridine (DMAP), and chloroform-d were supplied by Tokyo Chemical Industry. All materials were used as received.

Dye formulation

C. I. Disperse Red 1 (**1**) and carboxylic acid were combined to produce a Steglich esterification reaction [2] (Figure 6). The dye **3a** was synthesized from **1** using acrylic acid (**2a**), which contains a polymerizable group. The dye **3b** was synthesized using butyric acid (**2b**), which contains a non-polymerizable group. The dye **3a** is commercially available, while **3b** is a new dye.

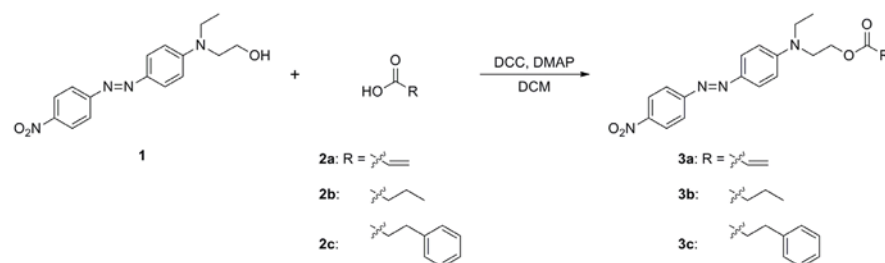


Figure 6: Synthesis of dye.

Material printing

The dyes were each added to UV varnish (acrylate 97wt%, photo-initiator 3wt%) with a concentration of 0.1 mol kg^{-1} to create inks, which were applied uniformly to different regions ($20 \times 4 \text{ cm}$) of white paper with a KRK universal printability tester (Kumagai Riki Kogyo) at a thickness of $3.0 \mu\text{m}$. The ink was cured under UV light with UV lighting equipment (Japan Storage Battery) using an 80 W metal-halide lamp. The radiation level (H) was varied (10 , 40 , and 640 mJ cm^{-2}). In this paper, prints made with inks containing **3a** and **3b** are referred to as 3A and 3B, respectively.

Color evaluation

The print colors were evaluated using a GretagMacbeth™ SpectroEye™ (Gretag-Macbeth AG) in a CIE $L^*a^*b^*$ color space. The evaluation was conducted under a D65 light source with an observation angle of 10° . Absolute white was used as the standard sample, and no built-in filter was used. The print properties were evaluated by calculating the color differences (ΔE^*) among them using

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (1),$$

where, between two prints, ΔL^* is the difference in brightness (L^*), Δa^* is the difference in the color coordinate a^* , and Δb^* is the difference in the color coordinate b^* . In this research, the isochromatic property and tamper-evident property were defined as outlined below.

(a) Isochromatic property

The value of ΔE^* between 3A and 3B irradiated with equal values of H ($H = 10, 40, 640 \text{ mJ cm}^{-2}$). When $\Delta E^* < 2.0$, 3A and 3B are evaluated as isochromatic.

(b) Tamper-evident property

The value of ΔE^* between 3A and 3B immersed in a solvent for equal values of t ($t = 0.5, 120 \text{ min}$). Prints irradiated with H ($H = 10, 40, 640 \text{ mJ cm}^{-2}$) were evaluated for ethyl acetate, and those irradiated with H ($H = 40 \text{ mJ cm}^{-2}$) were evaluated for acetone, toluene, dichloromethane, and ethanol. When $\Delta E^* > 5.0$, 3A and 3B were evaluated as having tamper-evident properties.

Results and discussion

Dye formulation

The dyes were obtained as reddish crystals.

Color evaluation

(a) Isochromatic property

Isochromatic behavior was maintained even as H increased, with values of $\Delta E^* = 1.1$ ($H = 10 \text{ mJ cm}^{-2}$), 0.5 ($H = 40 \text{ mJ cm}^{-2}$), and 1.1 ($H = 640 \text{ mJ cm}^{-2}$). This might suggest that the prints maintained isochromatic behavior even in a UV environment. Isochromatic behavior is attributable to chemical structures similar to those of **3a** and **3b**.

(b) Tamper-evident property

ΔE^* increased as H or t increased. At $t = 120 \text{ min}$, ΔE^* was 38.2 ($H = 10 \text{ mJ cm}^{-2}$), 43.1 ($H = 40 \text{ mJ cm}^{-2}$), and 21.1 ($H = 640 \text{ mJ cm}^{-2}$). The highest value ΔE^* was observed at $H = 40 \text{ mJ cm}^{-2}$ because higher values of H contribute to large ΔE^* values for 3A, while lower values contribute to large ΔE^* values for 3B. At $t = 0.5 \text{ min}$, $\Delta E^* = 12.0$ ($H = 40 \text{ mJ cm}^{-2}$), indicating tamper-evident property in the print

immediately after solvent immersion. For other solvents ($t = 120$ min), the print ($H = 40 \text{ mJ cm}^{-2}$) showed good tamper-evident property: $\Delta E^* = 43.5$ (acetone), 43.2 (toluene), $\Delta E^* = 42.7$ (dichloromethane), and 41.6 (ethanol).

Conclusions

In the work reported here, an isochromatic polymerizable dye **3a** and a non-polymerizable dye **3b** were used to address issues associated with isochromatic pair ink, such as the high level of expertise required for its manufacture and deterioration of isochromatic property due to dye decomposition. The dye **3a** dissolved less than the dye **3b** did thanks to stability gained from copolymerization with the UV varnish using its polymerizable unit, while **3b** dye did not have such stability. We believe that the method presented here is applicable to other dyes to produce isochromatic tamper-evident inks with various colors, widening the application of isochromatic tamper-evident inks.

References

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