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Reversible Thermochromic Ink based on Crystal Violet Lactone/Boric Acid/Hexadecyl Alcohol for Anti-Counterfeiting Printing

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Abstract. *The purpose of the study is to prepare reversible thermochromic materials with good discoloration properties, which are used as fillers to prepare a new type of reversible thermochromic ink. Reversible thermochromic materials were prepared by solid phase method with crystal violet lactone as chromogenic agent, boric acid as chromogenic agent and hexadecanol as cosolvent, and reversible thermochromic ink was prepared by using thermochromic material as filler. The scanning electron microscope images of reversible thermochromic materials showed that the prepared materials were spherical and had the advantages of non-adhesion. The printability of reversible thermochromic ink was discussed by changing the parameters including content of thermochromic material, printing pressure, ink sequence and using printability tester. The test of color change performance of thermochromic ink showed that the color change temperature range was 47.5–51.1°C, the color change time was 46 s, the recolor time was 29 s, and the stability was excellent. The reversible thermochromic ink has a certain application value in anti-counterfeiting printing.* © *2022 Society for Imaging Science and Technology.*
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1. INTRODUCTION

Thermochromic ink is a kind of ink which can change color under certain temperature. According to whether the thermochromic ink can be recovered after discoloration, it can be divided into reversible thermochromic ink and irreversible thermochromic ink. In recent years, thermochromic materials have been extensively researched because of their potential applications in anti-counterfeiting signs, temperature indicators, wearable electronic devices, medical diagnostics, safety materials, aerospace and other fields [1–8]. Thermochromic material has special thermal memory function, and the color of compounds and mixtures will change significantly during heating or cooling [9–13]. However, the thermochromic materials used in irreversible thermochromic inks mainly contain heavy metals, and their discoloration temperatures are high and performance unstable, so they are gradually replaced by reversible thermochromic inks. Currently, the main problems of reversible thermochromic inks are low sensitivity and poor color stability [14–16].

There are many organic reversible thermochromic materials, which can be divided into triphenylmethane, dianthrone, fluorane and spiro according to the structure of organic compounds. The mechanisms of organic reversible thermochromic materials mainly include electron gain and loss, coordination mode transformation, isomer mutual transformation and molecular chain thermal movement [17]. Currently, according to the different components of organic thermochromic materials, they are divided into two categories, one is the dominant thermochromic materials with a single component, and the other is thermochromic materials with multi-component composite system [18]. Because the thermochromic material of multi-component composite system has the advantages of obvious discoloration, low cost, sensitive discoloration and low discoloration temperature, it has become one of the most widely studied and promising organic thermochromic materials. Zhu et al. prepared crystal violet lactone by using N,N-dimethylaniline, p-dimethylanimobenzaldehyde and m-dimethylanimobenzoic acid. Thermochromic materials were prepared by the chelation reaction of crystal violet lactone and phenols, aromatic amines, carboxylic acids, and Lewis acids, respectively. Results indicated that the thermochromic materials had good reversible thermochromic behavior [19]. Li et al. put forward a novel way to fabricate the VO_2(B)/SnO_2 composite for preparing the thermochromic VO_2(M)/SnO_2 heterostructured film. It could be applied in smart windows [20]. Kamphan et al. prepared polydiacetylene (PDA)-based materials with reversible thermochromism by the incorporation of low molecular weight poly(vinylpyrrolidone) (PVP10) into the PDA assemblies. They prepared two-step color transition films by using the poly (PCDA)/PVP10 nanocomposite. It indicated reversible blue-to-purple at 90°C and reversible purple-to-red at 150°C [21]. Wang et al. designed a new type of microencapsulated phase change materials (microPCMs) with an additional function of thermochromic performance. The tests indicated that the materials could change their color as the temperature exceeded the target temperature. It showed great potential in applications for solar energy storage, thermo-sensors, food and medicine packages and intelligent textiles [22]. Zhang et al. prepared a reversible discoloration polyester fabric by dyeing with

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thermochromic white dye silica nanocapsules [23]. In addition, some thermochromic fibers can be obtained by spinning thermochromic pigments into molten polymers.

In this study, the reversible thermochromic material was prepared by solid phase method with crystal violet lactone as the color former, boric acid as the color developer and hexadecyl alcohol as the co-solvent. The test showed that the discoloration effect and stability were excellent. The discoloration temperature range was 47.5–51.1°C, from blue-green to colorless. In the process of reversible thermochromic material discoloration, the chromogenic agent determines the color of the compound system, the chromogenic agent is the organic compound that causes thermochromism, and the solvent determines the discoloration temperature of the material [24–26].

2. MATERIALS AND METHODS

2.1 *Materials*

Offset white ink and yellow ink were purchased from Tianjin Tiannu Chemical Group Co., Ltd (Tianjin, China). No. 1 ink compound was purchased from Guangzhou Yinyu Technology Co., Ltd (Guangzhou, China). 120 g/m^2 coated paper was purchased from Shenzhen Tiantai Hongyin Co., Ltd (Shenzhen, China). Hexadecanol, boric acid, crystal violet lactone, 2-ethylhexanol, ethyl acetate and isopropanol were purchased from Sinopharmaceutical Group Chemical Reagent Co., Ltd (Shanghai, China). Modified malic acid resin was purchased from Jiangxi Huajin New material Co., Ltd., and SRE-4190 hyperdispersant was purchased from Guangzhou Dong Fugui Chemical Raw Material Co., Ltd (Guangzhou, China).

2.2 *Experimental Scheme Design*

The discoloration performance and printability of thermochromic inks are greatly affected by the discoloration properties, particle size and content of thermochromic materials, while the printing pressure is also related to various optical properties of the samples, including the ink layer thickness and color difference of samples. Hence, it is particularly important to study the relationship between the chromatism, particle size, content of thermochromic materials, and color difference of samples.

2.3 *Preparation of Thermochromic Materials*

The mixtures of crystal violet lactone, boric acid and hexadecyl alcohol with different mass ratios of 1:6:40, 1:10:40, 1:15:40, 1:6:50, 1:10:50 and 1:15:50 were obtained by electronic balance. The mixture was stirred in a water bath and reacted at 80°C for 3 h, then the sample was placed for cooling. The thermochromic materials were obtained by drying for 6 h in a constant temperature drying box at 40°C, and they were ground to obtain the powder.

After the reversible thermochromic material was dried in a drying tower, it was heated in a thermostat at 20°C at the rate of 3°C/min. The color change process and discoloration temperature were observed by visual method. The chromism performance of reversible thermochromic material should be evaluated from the following three aspects.

(1) Discoloration temperature. It refers to the temperature at which a material changes color.
(2) The color recovery time. It refers to the time taken for a material to recover its original color after it has completely changed color and is placed at room temperature (20°C). Generally speaking, the shorter the recovery time of the material, the better the performance.
(3) Chromotropic sensitivity. It refers to the sensitivity of a material to color changes in the process of temperature change, usually measured by the color change temperature range or color change time. The discoloration time is expressed by Δt, that is, the chromotropic sensitivity is excellent when the Δt is less than 20 s, the chromotropic sensitivity is good when Δt is more than 20 s and less than 30 s, the chromotropic sensitivity is mediocre when Δt is more than 30 s and less than 40 s, and the chromotropic sensitivity is poor when the Δt is less than 20 s.

2.4 *Preparation and Proofing of Reversible Thermochromic Ink*

According to formulation design, modified malic acid resin 30%, ethyl acetate 13%, super dispersant 2%, isopropanol and deionized water 55%, and some volume of defoamer were used to prepare a mixed solution. A certain amount of modified malic acid resin and ethyl acetate and a small amount of 2-ethyl cyclohexanol were added to isopropyl alcohol and stirred for 6 h to get the mixing solution. Different amounts of thermochromic materials were added to the mixed solution respectively. Meanwhile, hyperdispersant was added, and the reversible thermochromic ink was obtained by using the ink mixer at 1200 rad/min for 2 h. The art paper samples under different printing pressures were obtained by using the printability tester under the printing pressure of 300 N, 500 N and 800 N, respectively. At the same time, for the same type of ink under 500 N printing pressure, the samples of different ink layer thickness were obtained by using printability tester under different ink feeding.

2.5 *Offset White Ink Proofing*

Offset printing inks were proofed by printability meter at printing pressures of 300 N, 500 N and 800 N, respectively, and the splines obtained were used as the control group of reversible thermochromic ink.

2.6 *Overprint Proofing*

Yellow ink is one of the four primary colors of printing, so it is chosen for overprint proofing. Reversible thermochromic inks with 2.5 g and 3.0 g thermochromic materials and offset yellow inks with the same mass were obtained by using electronic balance. Under the printing pressure of 500 N, the printing adaptability tester was used to make samples according to the order of reversible thermochromic ink and offset printing yellow ink and the printing color order was changed to obtain splines and to test the splines.

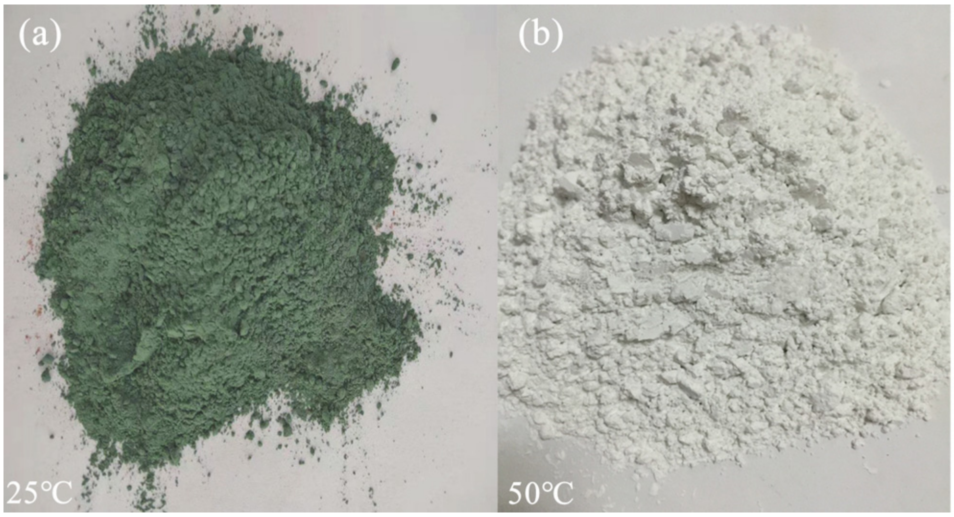


Figure 1. (a) Initial color at 25°C and (b) color after heating of the reversible thermochromic materials at 50°C.

Table I. Test of discoloration property of crystal violet lactone/boric acid/hexadecyl alcohol complex with different mass ratio.

Mass ratio	Color at 25°C	Color variation	Discoloration temperature/°C	Discoloration time/s	Color-recovering time/s	Discoloration effect	Reversibility
1:6:40	Light blue	Light blue → Colorless	45.7–49.1	43	25	Poor	Poor
1:10:40	Blue	Blue → Colorless	46.1–49.8	32	27	Mediocre	Mediocre
1:15:40	Dark blue	Dark blue → Colorless	47.2–50.2	29	32	Good	Mediocre
1:6:50	Light blue	Light Blue → Colorless	46.2–49.5	41	23	Mediocre	Poor
1:10:50	Blue	Blue → Colorless	46.8–50.1	32	25	Mediocre	Mediocre
1:15:50	Dark blue	Dark blue → Colorless	47.5–51.1	20	29	Excellent	Good

2.7 *Colorimetric Analyses*

In this experiment, the sample was analyzed mainly by using the spectrophotometer (X-rite 530) to measure the $L^*a^*b^*$ value of the sample at room temperature (20°C) and the $L^*a^*b^*$ value of the discoloration in the thermostat, so as to analyze the color difference ΔE^*, chromaticity difference Δa^* and Δb^* [27–30]. The total color difference and individual color difference of the two colors can be calculated by the following formula:

$$\Delta L^* = L_1{}^* - L_2{}^* \tag{1}$$

$$\Delta a^* = a_1{}^* - a_2{}^*; \quad \Delta b^* = b_1{}^* - b_2{}^* \tag{2}$$

$$\Delta E^*{}_{ab} = \left[\left(L_1{}^* - L_2{}^*\right)^2 + \left(a_1{}^* - a_2{}^*\right)^2 + \left(b_1{}^* - b_2{}^*\right)^2\right]^{1/2}. \tag{3}$$

When calculating the color difference, any one of them can be used as the standard color, then the other is the sample color. When the calculated results are positive or negative, the significance is as follows (assuming that sample 1 is the sample color and sample 2 is the standard color).

2.8 *Field Emission Scanning Electron Microscope (FE-SEM)*

The microstructure of the samples was obtained by using an FE-SEM (Gemini300, Carl Zeiss, Germany). First, the conductive tape is uniformly glued on the sample table, then a small amount of powder is applied on the tape, the particles that are not in contact with the tape are peeled off with the sample table down, and the weak powder is blown off gently with an ear-washing ball, so that a uniform layer of powder is left on the surface of the tape.

3. RESULTS AND DISCUSSION

3.1 *Test of Discoloration Properties of Reversible Thermochromic Materials*

The mass ratio among color former, color developer and co-solvent would affect the reversible thermochromic properties of discoloration compounds. In order to determine the best formula of reversible thermochromic materials, the comprehensive thermochromic properties of reversible thermochromic materials prepared with different mass ratios were tested as shown in the Table I. Figure 1 shows the initial color and discoloration of the sample when the mass ratio

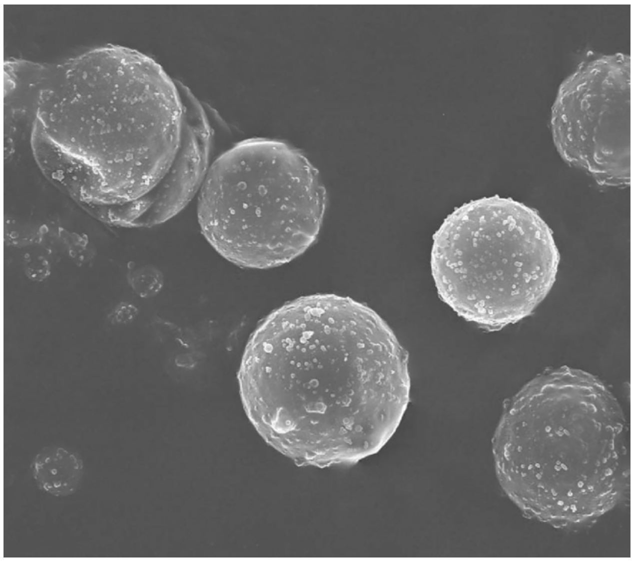


Figure 2. Scanning electron microscopy of the reversible thermochromic materials.

of crystal violet lactone, boric acid and hexadecyl alcohol is 1:15:50.

Table I showed that the thermochromic materials had the best performance when the mass ratio of crystal violet lactone, boric acid and hexadecyl alcohol was 1:15:50. It indicated dark blue at room temperature and became colorless at high temperature. The range of discoloration temperature was 47.5–51.1°C, discoloration time was 20 s, complex color time was 29 s, and the discoloration effect was excellent.

3.2 *Scanning Electron Microscopy Analysis of Reversible Thermochromic Materials and Characteristic Tests of Reversible Thermochromic Ink*

Reversible thermochromic materials vary in morphology, most of which are spherical. Their microencapsulated core may be composed of one or more substances. Wall materials are single and multilayer. Microcapsules formed by liquid capsules are usually spherical. If the core material is solid, the resulting microcapsules may be an irregular shape. Figure 2 is the SEM diagram of thermochromic materials. It showed that most of the thermochromic materials prepared in the experiment were spherical structures, and the obtained thermochromic materials have the advantages of relatively smooth surface and non-adhesion. It is conducive to reversible thermochromic ink heating more uniformly and with more rapid color change.

The performance of ink was tested by using scraping fineness meter and parallel viscometer. The fineness of reversible temperature-sensitive discoloration ink was 15 mm, the viscosity value was 14, and the fluidity was 22 mm. It met the standard of offset printing ink.

3.3 *Effect of Printing Pressure and Thermochromic Material Content on Color Difference*

According to a large number of studies, it is difficult for the human eye to distinguish the color difference which is less than 1.5, and it can obviously distinguish the color difference that is greater than 2.4 [31, 32]. The figures (Figure 3 and 4) indicated that the color change of the sample became more obvious with the increase of pressure.

Table II. Effect of reversible thermochromic materials content and printing pressure on color difference of samples.

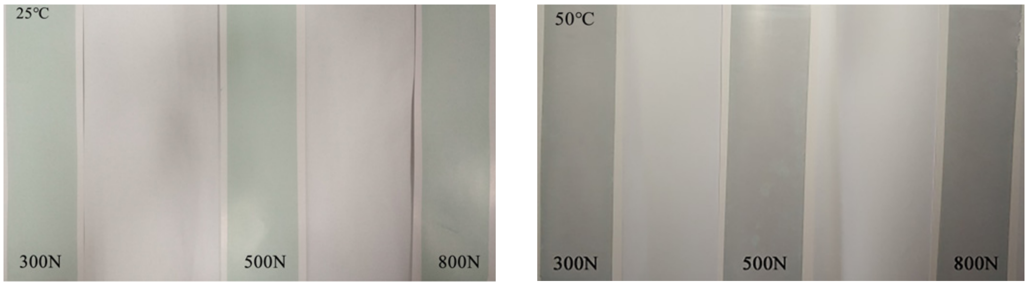
Thermochromic material content/%	Printing pressure/N		
	300	500	800
20	5.12 ± 0.11	6.35 ± 0.18	7.56 ± 0.21
25	7.71 ± 0.18	8.66 ± 0.17	10.14 ± 0.20
30	7.13 ± 0.24	8.16 ± 0.23	8.95 ± 0.23
35	6.82 ± 0.23	7.97 ± 0.25	8.68 ± 0.26
40	6.24 ± 0.28	6.48 ± 0.26	7.17 ± 0.30

The results (Table II) indicated that the color difference was the smallest under three kinds of printing pressure when the content of reversible thermochromic materials in reversible thermochromic ink were 20% and 40%. The transfer performance of the ink was excellent, when the content of reversible thermochromic materials was 25% to 35%. Therefore, the reversible thermochromic ink had better thermochromic performance. When the content of reversible thermochromic materials was more than 35%, the transfer performance of ink was affected by the content of thermochromic materials, the transfer amount of ink decreased, the corresponding reversible thermochromic materials and the discoloration effect decreased.

In Figure 5, the change of color difference increased gradually in the range of 25% to 30%, and then decreased. When the content of reversible thermochromic materials reached 40%, the transfer performance of the prepared reversible thermochromic ink decreased, and more reversible thermochromic materials remained on the drum of the printing adaptability meter, affecting the thickness and integrity of the ink layer of the spline. Meanwhile, the color difference of ink with the same content of reversible thermochromic materials increased gradually with the increase of printing pressure, but when the content of reversible thermochromic materials reached 40%, the color difference decreased with the increase of printing pressure. It was because the printing pressure exceeded the upper limit of reversible thermochromic materials, and the particle capsule of reversible thermochromic materials broke, which affected the discoloration performance of reversible thermochromic ink, even if the temperature changed, it was difficult to make the spline change obviously.

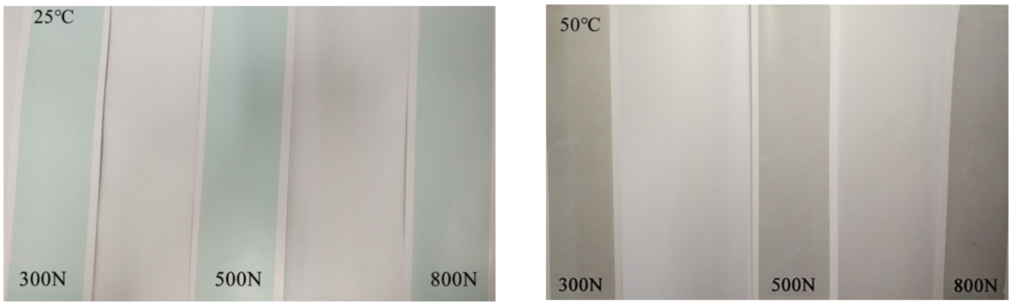
3.4 *Effects of Content of Reversible Thermochromic Materials and Ink Layer Thickness on Discoloration Properties and Solid Density*

The results (Table III, Figure 6 and Figure 7) showed that the color difference of the sample gradually increased as the ink feeding amount increased, but when the ink feeding amount was more than 0.7 ml, the increase in color difference



(a) Without discoloration（cyan） (b) Discoloration（offwhite）

Figure 3. Comparison of colors for 25% thermochromic inks at 25°C and 50°C



(a) Without discoloration（cyan） (b) Discoloration（offwhite）

Figure 4. Comparison of colors for 30% thermochromic inks at 25°C and 50°C.

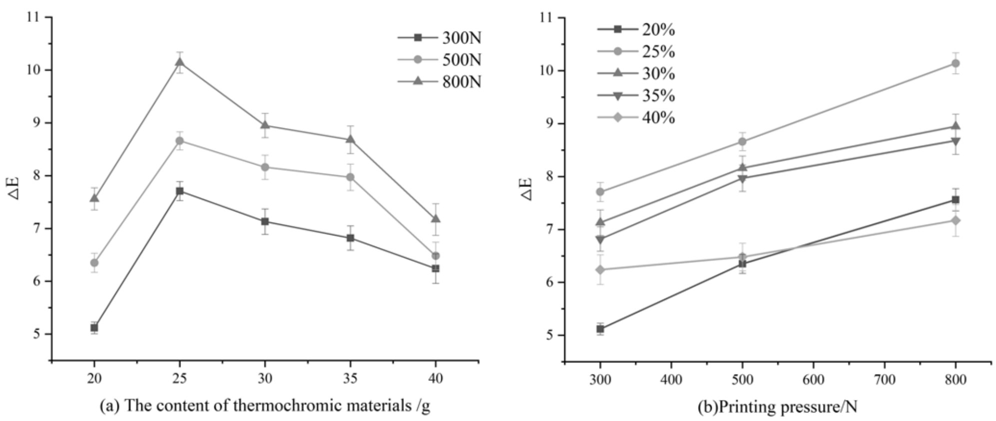


Figure 5. Effect of (a) the content of thermochromic material and (b) printing pressure on color difference of samples.

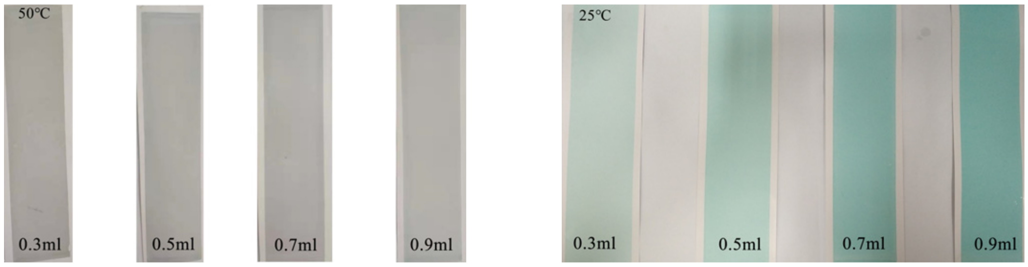
Table III. Effect of ink layer thickness on color difference.

The content of thermochromic materials/%	Amount of ink injection/ml			
	0.3	0.5	0.7	0.9
20	5.81 ± 0.23	13.15 ± 0.27	19.32 ± 0.34	20.42 ± 0.31
25	9.33 ± 0.34	17.53 ± 0.31	25.83 ± 0.38	29.13 ± 0.34
30	4.92 ± 0.31	12.04 ± 0.35	17.94 ± 0.37	22.81 ± 0.39

significantly decreased. The reason was that the amount of ink transfer had a certain upper limit. When the amount of ink feeding exceeded the limit, the amount of ink transfer would be significantly reduced, so the amount of ink in the printing process was also an important factor affecting the quality of printing. Therefore, keeping the content of reversible thermochromic materials in an appropriate range could ensure the discoloration performance of reversible thermochromic ink, and the ink feeding had a great influence on the temperature-sensitive color change of the samples. It could effectively control the ink cost and ensure good printability.

3.5 *Reversible Thermochromic Ink Overprinting Effect*

From the Table IV, it could be seen that the values of L^*, a^*, and b^* of the sample changed slightly at 50°C. Among them, the upward trend of L^* value was evidence



(a) Without discoloration (b) Discoloration

Figure 6. Discoloration effect of thermochromic ink with different amount of ink feeding (at 25°C and 50°C)

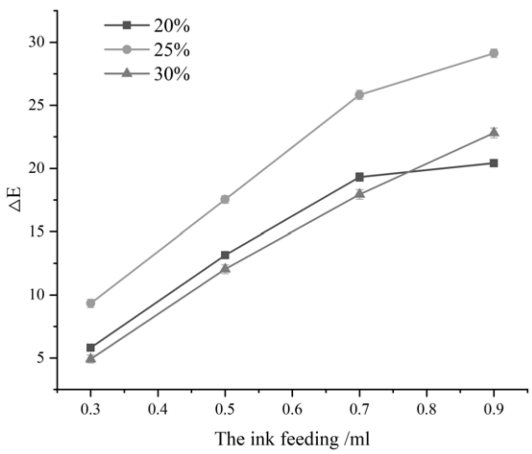


Figure 7. Effect of ink layer thickness on color difference.

Table IV. *$L^*a^*b^*$ value after changing the overprint order of the sample.*

Overprint sequence	Reversible thermochromic ink on top of offset yellow ink		Offset yellow ink on top of reversible thermochromic ink	
	25%	30%	25%	30%
Mean value of L^*	75.07 ± 0.21	77.11 ± 0.37	77.82 ± 0.18	78.29 ± 0.31
Mean value of a^*	-3.53 ± 0.11	-3.20 ± 0.13	-6.11 ± 0.16	-6.07 ± 0.28
Mean value of b^*	52.74 ± 0.24	53.86 ± 0.26	86.56 ± 0.31	88.75 ± 0.34

that the color surface of the sample became brighter as the reversible thermochromic materials increased, and that the a^* value decreased as the content of the thermal discoloration material increased, indicating that the green color of the sample was more obvious. However, the change of a^* value was smaller than the b^* value, indicating that offset yellow ink had a certain masking effect on the color performance of reversible thermochromic ink, which would affect the color performance of reversible thermochromic ink. When the overprinting order changed, the change of the b^* value on the sample indicated that reversible thermal discoloration ink had a poor color-blocking effect on other inks. At the same time, the increase of reversible thermochromic materials would not increase the color masking effect of thermochromic ink. Therefore, the reversible thermochromic ink prepared by reversible thermochromic material synthesized from crystal violet lactone/boric acid/hexadecyl alcohol was not suitable for anti-counterfeiting printing by overprinting.

4. CONCLUSION

In this work, a series of different mass ratio reversible thermochromic materials were prepared by solid phase synthesis method, choosing hexadecyl alcohol as the co-solvent, crystal violet lactone as chromophoric reagent and hexadecyl alcohol as delomorphic reagent. This work studied the best mass ratio (quality ratio) of the chromophoric reagent and the solvent on the properties of reversible thermochromic materials. When the mass ratio of crystal violet lactone, boric acid and hexadecyl alcohol was 1:15:50, the thermochromic material had the best performance. It showed dark blue at room temperature and became colorless at high temperature. The discoloration temperature range was 47.5–51.1°C, discoloration time was 20 s, complex color time was 29 s, and the discoloration effect was excellent. In addition, it is found that overprint will reduce the discoloration performance of reversible thermochromic ink, thereby affecting its anti-counterfeiting performance. This work contributes a novel strategy of developing reversible thermochromic materials with color-changing performance and anti-counterfeiting applications for intelligent packaging and intelligent sensor. The effects of solvent, stirring rate, stirring time and microencapsulation on the complex system color sensitivity, color stability and color time will be studied in the follow-up, so as to further promote its application in anti-counterfeiting packaging.

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