Reversible Thermochromism Materials Micro-Encapsulation and Application in Offset Printing Ink

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Abstract: By repeating experiments, the preparation technological conditions of microcapsule were determined considering their respective optimal compositions of the core and shell of microcapsule, and other factors. And some properties of reversible thermochromic materials and microcapsules were studied including the resisting capabilities of fatigue and oxidation, the stability to chemical ambiences such as acid, alkali and solvents, etc. By experiment equipment, this paper prepared the reversible thermochromism material in offset printing ink, and discussed the printability of reversible thermochromism off-set printing ink. By spector photometer, measured the L a b value, chromatism, and anti-counterfeiting properties of off-set printing ink of reversible thermochromism ink under off-set printing pattern. This paper has theoretical direction function in anti-forgery ink of reversible thermochromism material.

Keywords: Microcapsule, Reversible thermochromic materials, Offset printing ink

1. Introduction

Microencapsulation technology is a film-forming material with the solid or liquid or gaseous coating, so that the formation of tiny particles of Technology. The tiny particles are called microcapsules[1]. In this paper， experiments on the reversible thermochromic material optimized microencapsulation process, and measured it characteristics. By experiment prepared the reversible thermochromism material in offset printing ink, and discussed the printability of reversible thermochromism off-set printing ink.

2. Materials and instrument

2.1 **Materials**

procrypsis dye, hexadecanol, BPA(bisphenol A), Gelatin, Gum Arabic, urea-formaldehyde resin, formaldehyde，ammonia, white gloss set offset printing ink, 120g coated paper. Experimental water was distilled water，Conductivity of 6 to 8 ohm -1 / cm.

2.2. Main experimental instrument

XMTB type Digital temperature water bath，Beijing Changfeng instrumentation company.

Multi-functional electric speed mixer：D-8401 type.

BEIDESH-5 Magnetic mixer

The American BRUKE company produced VECTOR22 infrared spectrometer.

X-Rite528 Spectrophotometer

PHS－3C PH meter

IGT2C1 Printability Tester，Printing speed 0.3m/s，Printing pressure between 100 and 1000N.

Refilling device：IGT C1，Maximum capacity $2cm^3$

3. Reversible Thermochromism materials Microencapsulation

The experiment found that affect the temperature Thermochromism microcapsules of factors, including: the choice than the core of a capsule wall, the wall material of choice, time of emulsification, etc. The following respectively discussed these factors.

3.1 The Impact of emulsification time on the average particle size of microcapsules

In order to form a stable emulsion, High-speed mixing （2000 r / min）plays a very big role in dispersion. If the effect of mechanical dispersion was better, the core of a capsule size smaller, surface area larger, surface tension smaller, and emulsions more stable. The results were shown as table 1.

Table1：Emulsification time on the average particle size of microcapsules

Section No.	1	2	3	4	5	6
Emulsification time (min)	5	10	15	20	25	>30
The average particle size capsules (um)	700	200	100	40	35	<25

As can be seen from Table 1, select high-speed emulsion for 30 minutes, a more uniform particle size less than 25um and microcapsules was obtained.

3.2 The Impact of microcapsule-wall preparation of prepolymer on structure of the microcapsules

The Impact of microcapsule-wall preparation of prepolymer on structure of the microcapsules as shown in Table 2:

Table2: Microcapsule-wall preparation of prepolymer solution of formaldehyde / urea molar ratio of the micro-capsule structure

Section No.	1	2	3	4	5	6
Preparation of prepolymer solution (Formaldehyde / carbamide)	0.5	1.0	1.5	2.0	2.5	3.0
Microcapsule structure	Very poor	good	Very good	good	Had agglomerate phenomenon	agglomerated

As can be seen from Table 2, in the Microcapsule-wall preparation of prepolymer, the best ratio of urea and formaldehyde was 1.5:1.

3. 3 Different microcapsule-wall material and microcapsule-core after microencapsulation comparison

As can be seen from Table 3, with procrypsis dyes: color reagent: solvent 1:3:40 (weight ratio) of the microcapsule -core, with different microcapsule-wall materials of the microcapsules produced different results. The best of results was with urea and formaldehyde copolymer made of microcapsule-wall material microcapsules, and good separation of the formation of microcapsules. Therefore, in subsequent experiment, only for urea and formaldehyde copolymer to do when the microcapsule-wall material synthesis did detailed research.

Table3: Different microcapsule-wall material and microcapsule-core after microencapsulation comparison

microcapsule -wall material	microcapsule -core material	Microcapsule structure	Segregation
Urea and formaldehyde copolymer	procrypsis dye, color agent and solvent, 1：3：40	Very good	Easily separated
Gelatin and gum arabic	procrypsis dye, color agent and solvent, 1：3：40	Better	Hardly separated

3.4 The ratio of microcapsule–core and microcapsule -wall

The ratio of microcapsule–core and microcapsule-wall will affect the effect of the emulsion, microcapsule particle size, color changes intensity and sensitivity of micro-capsules. The experiments were selected microcapsule–core with microcapsule-wall ratio 1:1, 1:1.5, 1:2, 1:2.5, 1:3 preparation of microcapsules. The results were shown in table 4.

Table4 The impact of the ratio of microcapsule–core and microcapsule–wall on microcapsule properties

proportion	1:1	1:1.5	1:2	1:2.5	1:3
Color change	Red	light red	Light red	Red	Near light red
Differences in particle	Clustered in large	Clustered in small	less	powder	Particle aggregation
Change effects	Poor	Poor	better	good	poor
Conversion	31.4%	38.02%	35.59%	59.5%	57.1%

Note: The ratio of microcapsule–core and microcapsul –wall is weight ratio

As can be seen from Table 4, the best ratio of microcapsule–core and microcapsule–wall was 1:2.5. Under these conditions, it can cause the highest yield of microcapsules, better color change effect, and higher color changes intensity.

4. Microcapsule product and not the encapsulated thermochromism material, acid and alkali resistance compared

Microcapsule product and not the encapsulated thermochromism material of acid and alkali test was shown in table 5.

In the experiment, the common organic solvents, acids, alkalis, common detergent and hot water were selected on the test of properties of the reversible thermochromism microcapsules products and not the encapsulated reversible thermochromism material.

As can be seen from Table 5, in resistant to organic solvents, acids, alkalis, common detergent and hot water, microencapsulated products was better than not the encapsulated reversible thermochromism material. So the reversible thermochromism materials must be microencapsulated processing.

Table 5: Micro-capsule product and not the encapsulated thermochromism material temperature solvent, acid and alkali resistance test

Microcapsule product solvent, acid and alkali resistance test						
solvent	Test temperature ℃	Test Time (min)	dissolvability		Color change	
			Micro-capsules	Thermo-chromism materials not micro-encapsulation	Micro-capsules	Thermo-chromism materials not micro-encapsulation
benzene	25	60	indissolvableness	dissolve	No change	achromatic color
toluene	25	60	indissolvableness	dissolve	Lighter	achromatic color
xylene	25	60	indissolvableness	dissolve	No change	achromatic color

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chloro-form	25	60	indissolv-ableness	dissolve	Lighter	achromatic color
acetic acid (20%)	25	60	indissolv-ableness	indissolv-ablenes	No change	No change
sulphuric acid (2%)	25	60	indissolv-ableness	indissolv-ablenes	No change	No change
hydro-chloric acid (10%)	25	60	indissolv-ableness	indissolv-ablenes	No change	No change
NaOH（2%）	40	60	indissolv-ableness	indissolv-ablenes	Lighter	Lighter
					Non-resume on normal tempera-ture	resume on normal temperature
wash-ing-powder（2%）	40	60	indissolv-ableness	indissolv-ablenes	Lighter	Lighter
					resume on normal tempera-ture	resume on normal temperature
soap (10%)	80	60	indissolv-ablenes	indissolv-ablenes	deepen	deepen
					resume on normal tempera-ture	
acetone	25	60	indissolv-ablenes	dissolve	Slightly lighter	achromatic color
ethanol	25	60	indissolv-ablenes	indissolv-ablenes	Lighter	Lighter
Hot water	80	60	indissolv-ablenes	indissolv-ablenes	Lighter	Lighter
					resume on normal tempera-ture	resume on normal temperature

5. Reversible thermochromism materials in the application of offset printing ink

5.1 Reversible thermochromism ink proofing

The different weights of the above microcapsules were reversibly thermochromism material to white gloss set offset printing ink. Using the printability tester make the proof at three kinds of printing pressure (250N, 500N, 800N).

5.2 The impact of printing pressure on reversibly thermochromism offset printing ink

Offset printing pressure is important factor, and it is a greater impact on the ink film thickness. The Figure 1 shows that, with the printing pressure increases significantly increased color change, but when the ink film thickness saturated, even if the printing pressure, no significant changes in color.

In offset printing process, the printing pressure can not be too large to prevent the materials reversibly change microcapsule–core.

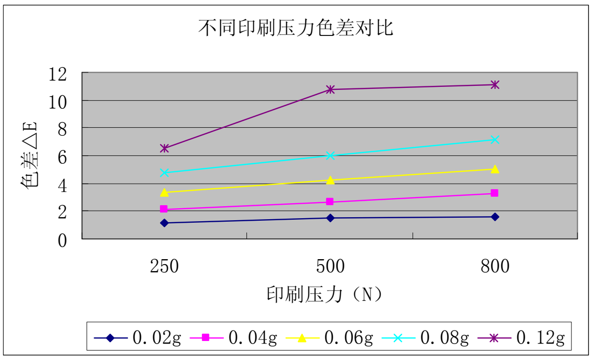

Figure 1 Comparison of chromatism of different printing pressure

5.3 The trapping effects of reversible thermochromic offset printing ink

Firstly, under the printing pressure of 500N according to the order of the yellow ink – reversible thermochromic printing ink completed proofing. Then using the opposite order completed the second proofing.

As can be seen from Table 6, in the data of $L^* a^* b^*$, the biggest change for the b^* value. The b^* value is larger, higher value on behalf of yellow. It is just consistent with the printing proofs.

In the first trapping order, it is obvious to see the color of reversible thermochromic printing ink, and at a certain temperature, to reflect the occurrence of discoloration. In the second trapping order, the reversible thermochromic printing ink was covered by yellow ink, so at a certain temperature, the human eyes is hard to see the changes in color.

Table 6: The Value of $L^* a^* b^*$ of different trapping sequence

	First Yellow ink After reversible thermo-chromic printing ink(0.12g reversible thermo-	First Yellow ink After reversible thermo-chromic printing ink(0.3g reversible thermo-	First reversible thermo-chromic printing ink After Yellow ink(0.12g reversible thermo-	First reversible thermo-chromic printing ink After Yellow ink(0.3g reversible thermo-

	chromic materials)	chromic materials)	chromic materials)	chromic materials)
L^* mean-value	84. 15	73. 99	76. 52	71. 52
a^* mean-value	8. 84	20. 43	15. 97	21. 31
b^* mean-value	5. 28	3. 83	81. 1	72. 85

6. Conclusion

6.1 In the Microcapsule-wall preparation of prepolymer, the best ratio of urea and formaldehyde was 1.5:1.

6.2 The best ratio of microcapsule–core and microcapsule–wall was 1:2.5. Under these conditions, it can cause the highest yield of microcapsules, better color change effect, and higher color changes intensity.

6.3 In resistant to organic solvents, acids, alkalis, common detergent and hot water, microencapsulated products was better than not the encapsulated reversible thermochromism material.

6.4 In offset printing process, the printing pressure can not be too large to prevent the materials reversibly change microcapsule–core.

6.5 Reversible thermochromism offset printing ink is not suitable overprint mode, and the best way is use of homochromatism printing can reached the security printing results.

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