EFFECT OF PAPERMAKING CONDITIONS ON THE RETENTION OF REVERSIBLE THERMOCHROMIC MICROCAPSULE IN PAPER

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Reversible thermochromic paper able to resist counterfeiting was prepared by adding reversible thermochromic microcapsules (RTM) to a slurry of cellulosic fibers, a process that is difficult to imitate. However, the loss of RTM is one of the biggest problems that inhibits industrial use of this approach. So, the retention of RTM in pulp was investigated. The RTM was synthesized by in-situ polymerization, and its properties were characterized. It exhibited strong color contrast between cool and heated conditions, and such behavior could be used to achieve distinctive anticounterfeiting characteristics in the paper. The surface of each microcapsule was smooth, and there was no coherence between particles. The diameters of the microcapsules were mainly in the range 3.0 μm to 5.0 μm. Retention of RTM was closely related to beating degree and pulp composition; the higher the beating degree and hardwood pulp content, the higher the retention of RTM. On the other hand, the retention of RTM was influenced by filler and retention aid. Retention aid promoted retention of RTM to some degree; however, filler was not conductive to retention of RTM. Different addition sequences between RTM and filler or retention aid also influenced the retention of RTM.

Keywords: Reversible; Retention; Beating; Hardwood; PCC

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INTRODUCTION

Reversible thermochromic material changes color when heated, but it reverts to its original color on cooling. Organic reversible thermochromic complexes have become increasingly important in recent years for uses in textiles and smart coatings (Favaro and Masetti 1994). In particular, organic complexes with electron donor, electron acceptor, and solvent are commonly used in consumer applications (Zhu and Wu 2005) because the temperature at which they change color is often within the temperature range of the living environment. Its application has been extended to many fields, such as toys, temperature indicators, and printing inks (Ma and Zhu 2000). However, very little attention has been paid to the study of reversible thermochromism in the papermaking industry. In principle, reversible thermochromic anti-counterfeiting paper can be exploited by addition of the reversible thermochromic material to a pulp suspension. But such an approach is likely to result in undesirable consequences when the complexes are added directly to the fibrous slurry, a situation that can limit commercial interest in such applications.

Microcapsulation technology has revolutionized the application of reversible thermochromic material; however the first industrialization of microencapsulation technology was realized in the manufacture of pressure-sensitive copying paper. Microcapsulation is very popular in many fields for it can offer superior functions, such as isolation of reactant, protection of volatile material, protection from humidity and oxygen, safe handling of toxic materials, and confinement of taste and odor.

The reversible thermochromic anti-counterfeiting paper could be prepared by a coating method or by adding RTM into pulp at the wet-end of a paper machine, but there are considerable differences between the two methods. The former method could save consumption of reversible thermochromic capsule, and the later method could achieve an effect that was difficult to imitate by other means due to the unavailability of papermaking equipment to most potential counterfeiters. However, the loss of RTM due to its non-retention in the paper is inevitable during this process. So, the objectives of the present work were to find which process conditions of papermaking influenced the retention of RTM. This is expected to provide some valuable information to aid in understanding the retention mechanism of RTM and also provide a favorable basis for the optimization of the technology.

EXPERIMENTAL

Material and Chemicals

Hardwood (eucalyptus) bleached kraft pulp (HWBKP) and softwood (spruce) bleached kraft pulp (SWBKP) were obtained from a pilot mill. Softwood pulp was used for all experiments in this study unless specified. Papermaking grade PCC (precipitated calcium carbonate) with ISO brightness of 92% was supplied by Shandong Huatai Co., Ltd.; its mean diameter was tested to be 2.4 µm. Cationic polyacrylamide (CPAM) with molecular weight of 5 million was supplied by Huatai Co., Ltd., and it was used as retention aid. Urea, formaldehyde (37% aqueous solution), triethanolamine, and tetradecyl alcohol provided by Tianjin Chemical Plant, China, were all reagent grade. The RTM was synthesized in lab by in-situ polymerization.

Encapsulation of the Reversible Thermochromic Material

(1) Preparation of UF (urea-formaldehyde) resin prepolymer

4 mol of urea and 6 mol of formaldehyde were placed into a three-necked flask, and 2% triethanolamine aqueous solution was added to adjust pH value to 8. The mixture was stirred for 1h at 70 ^{o}C until it became a transparent solution.

(2) Preparation of reversible thermochromic complexes

Leuco dye, bisphenol A, and tetradecyl alcohol were put in a three-necked flask, and then heated to 70 ^{o}C slowly. After stirring for 1.5 h at 70 ^{o}C, the mixture was cooled to room temperature. A reversible thermochromic complex was obtained.

(3) Preparation of UF microcapsules with reversible thermochromic complex core

Prepolymer and reversible thermochromic complex core were added into a three-necked flask at a given proportion, then heated slowly to 50 °C. The mixture was stirred vigorously for 30 min at 50 °C with an emulsifying apparatus after emulsifier was added. The resultant emulsion was stirred for 2h at 70 °C with an agitator, and ammonium chloride was added to adjust the pH value during this time. The final pH value was controlled at about 4. In order to avoid the reaction taking place too fast and adversely influencing the morphology and property of the microcapsules, the ammonium chloride were added slowly and for several time intervals. The obtained microcapsules were centrifugated and washed to neutral with purified water and then dried in an oven to constant weight.

Beating of Pulp

Pulp samples were beaten in a PFI mill at 10% stock consistency. The interspace between beating roll and beating chamber was 0.18 mm, and the load applied during refining was 3.4 N/mm.

Analysis of Fiber Quality

Analysis of fiber quality was performed in Fiber Quality Analysis of OpTest Company.

Preparation of RTM Suspension

The RTM sample was diluted to 0.3% with distilled water. To prevent it from flocculating and to distribute it equably in the paper, the microcapsule suspension was shaken before using and added to the pulp stock quickly.

Preparation of Handsheets

The pulp samples were disintegrated for 10,000 revolutions in a standard disintegrator at 1.5% , and then diluted to 1% . The required amount of pulp suspension was transferred to a 1000 mL beaker. Stirring with an adjustable speed mixer, the needed chemicals, such as RTM, PCC, AKD, and CPAM were successively added into the furnish. Handsheets were prepared with a Rapid Köthen apparatus using tap water. The basis weight of the paper was 60 gsm. Before testing, all the samples were kept at 23 °C and 65% rh for 24 h before further testing.

Determination of Chromatic Aberration

The retention of RTM in pulp had a direct relation to the value of chromatic aberration, so the retention of RTM was measured indirectly by the chromatic aberration of the paper. The determination of chromatic aberration was based on the CIELAB system. The determination of chromatic aberration was based on CIELAB system, its formula was $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$, where ΔE^* is chromatic aberration, L^*, a^*, and b^* were measured in a colorimeter (Elrepho 070, L&W Ltd) respectively. If the L^*, a^*, and b^* of standards sample were L_1^*, a_1^* and b_1^* respectively, and the L^*, a^*, and b^* of sample were L_2^*, a_2^*, and b_2^*, respectively, then $\Delta L^* = L_2^* - L_1^*$, $\Delta a^* = a_2^*$

$-a_1^*$, and $\Delta b^* = b_2^* - b_1^*$. The paper with same condition and furnishes but no RTM was the standard sample.

SEM Analysis

Scanning electron microscope (SEM) analysis was carried out on Nippon Electronic Company JSM-6460LV SEM.

RESULTS AND DISCUSSION

Properties of RTM

Fundamental properties and photomicrograph of RTM are shown in Table 1 and Fig. 1, respectively. Red RTM samples lost their color when heating up to 33 ^{o}C and changed into white. The strong color contrast between cool and heated conditions indicated a promise for preparation of anticounterfeiting paper.

Table 1. Fundamental properties of RTM sample

Complex of microcapsule core	electron donor	leuco dye
	electron acceptor	bisphenol A
	solvent	tetradecyl alcohol
Wall material	urea-formaldehyde resin	
Color change	red to white	
Temperature of color change	33 ^{o}C	
Zeta potential	0 mv	

The mass ratio of electron donor, electron acceptor, and solvent was 1:4:40.

In order to reliably confirm the encapsulation effect of reversible thermochromic materials and understand the morphology of RTM, SEM observation was conducted.

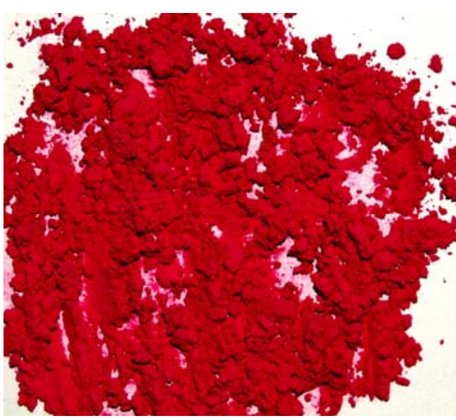

Figure 1. Picture of the RTM

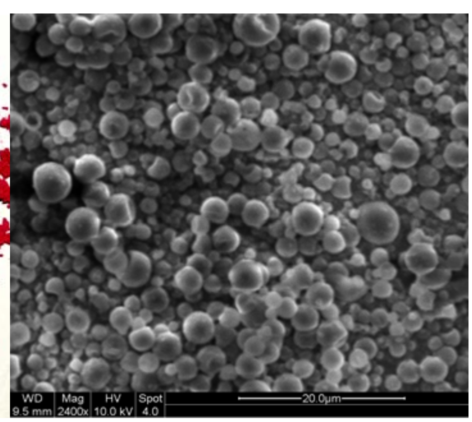

Figure 2. SEM image of RTM

An SEM image of the microcapsule is shown in Fig. 2. The surface of the microcapsule was smooth, and there was no adhesion between particles. On the other hand, the microcapsule showed some round-shaped features, and its diameter was mainly in the range of 3.0 to 5.0 µm, with an average diameter of 4.1 µm (Fig. 3).

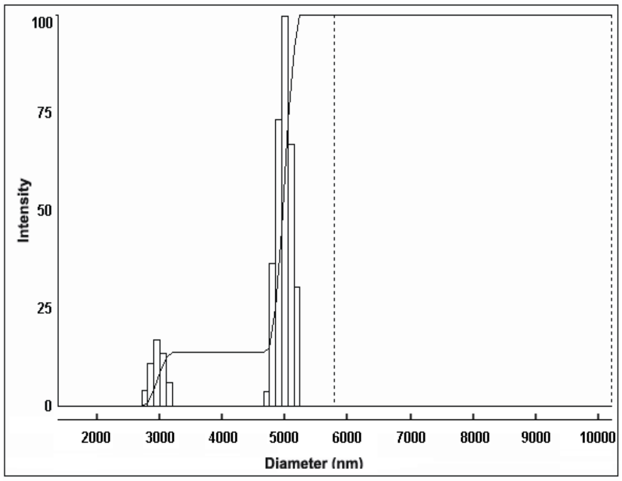

Figure. 3. Size distribution of microcapsules

Quantifying the Dosage of RTM in Paper

Due to the high cost of RTM, the dosage of RTM should be kept as low as possible, while still achieving sufficient chromatic aberration of paper, i.e. exhibiting a clearly visible effect. The effect of RTM dosage on chromatic aberration is shown in Table 2.

Table 2. Effect of RTM Dosage on the Chromatic Aberration of Paper

RTM dosage, %	Paper side	L*	a*	b*	Chromatic aberration	Chromatic aberration difference of paper sides
0	Felt side	94.24	0.78	2.16	0	0
	Wire side	93.95	0.65	3.29	0	
0.3	Felt side	91.57	4.40	0.60	4.76	1.15
	Wire side	91.11	5.10	0.63	5.91	
0.6	Felt side	89.98	6.86	-1.62	8.33	2.64
	Wire side	89.16	8.46	-2.74	10.97	
0.9	Felt side	88.78	8.44	-2.55	10.52	3.42
	Wire side	87.62	10.63	-4.10	13.94	
1.2	Felt side	87.33	9.76	-2.76	12.35	3.52
	Wire side	85.84	12.31	-3.80	15.87	
1.5	Felt side	86.69	10.41	-2.94	13.26	4.16
	Wire side	84.93	13.42	-4.39	17.42	

Note: the paper with same condition and furnishes but no RTM is standard sample.

The relation between digital chromatic aberration and visual chromatic aberration is shown in Table 3. It was apparent that only when the number of digital chromatic aberration was higher than 6, the visual requirements could be significantly met. For reversible thermochromic paper, chromatic aberration is one of the most important indexes and should be increased as high as possible in practice. As shown in Table 2, when the dosage of RTM was 0.6% (by wt), the chromatic aberration of paper could reach as high as 8.33, which could significantly meet the visual requirements, and the chromatic aberration increased gradually with the increasing of RTM dosage. Considering the effect of chromatic aberration and the cost of manufacture, the dosage of RTM was chosen to be about 0.6%, and all the subsequent experiments were done at this level.

Table 3. Relation between Digital Chromatic Aberration and Visual Chromatic Aberration

Chromatic aberration	Visual degree
0.0-0.5	pinpoint
0.5-1.5	slight
1.5-3.0	obvious
3.0-6.0	very obvious
above 6.0	intense

On the other hand, it was also found that the chromatic aberration of the wire side was higher than that of felt side, and this difference became more obvious with the increasing of RTM dosage. This might be related to the retention behavior of RTM in pulp. The dewatering process of pulp is illustrated in Fig. 4; under the action of filtration

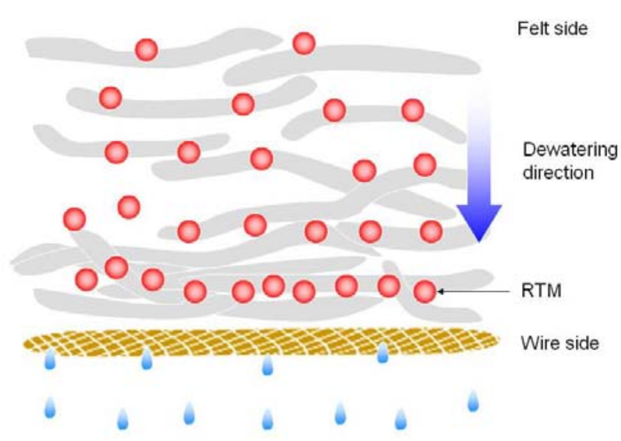

Fig. 4. Schematic diagram of dewatering during papermaking

and shear forces, the amount of RTM deposited within the sheet will increase gradually from felt side to wire side. With more RTM added, there is even more opportunity for it to be deposited on the wire side.

Retention of RTM in Paper

(1) Effect of beating on the retention of RTM

Beating is a mechanical treatment applied to improve physical properties and sheet formation in the manufacture of paper. Many theories have been developed to explain effects of beating on the fiber cell wall structure and surface morphology (Fardim and Duran 2003). Consistent conclusions have been reached that beating can promote fibrillation of fiber and cause delamination of surface layers.

Table 4. Effect of Beating Degree on the Retention of RTM

Beating revolutions, r	5000		10000		15000		20000	
Beating degree, °SR	19.0		37.3		40.5		53.0	
Paper side	Felt side	Wire side	Felt side	Wire side	Felt side	Wire side	Felt side	Wire side
L*	94.87	94.78	93.30	93.14	91.19	90.82	90.56	90.10
a*	0.97	1.12	2.18	2.45	5.63	6.31	6.86	7.65
b*	-0.18	-0.12	-0.36	-0.28	-0.44	-0.78	-0.81	-1.19
Chromatic aberration	3.2	3.5	5.0	5.1	8.0	8.9	9.5	10.5

The effect of beating degree on the chromatic aberration is shown in Table 4. Obviously, chromatic aberration of pulp with highbeating revolution was higher than that of pulp with low revolution. When beating revolution increased from 5000 r/m to 20000 r/m, the chromatic aberration could be improved as much as three times. On the other hand, higher beating degree gave the best contribution to the higher fines content and shorter length weighted mean length, both of which could facilitate the increase of surface area. It has been proved that the adsorption of fines considerably correlates with surface area. So, the significant improvement in chromatic aberration as a result of increasing beating degree was principally thought to be due to the increasing of surface area of fiber.

Figure 5, an SEM image, shows the distribution of RTM in pulp with different beating degree. The image indicates that RTM rested mainly on the fibers having higher degree of fibrillation. The greater the roughness of the fiber surface, the higher was the retention of RTM. Roughness was also closely related to beating; it increased with the beating extent.

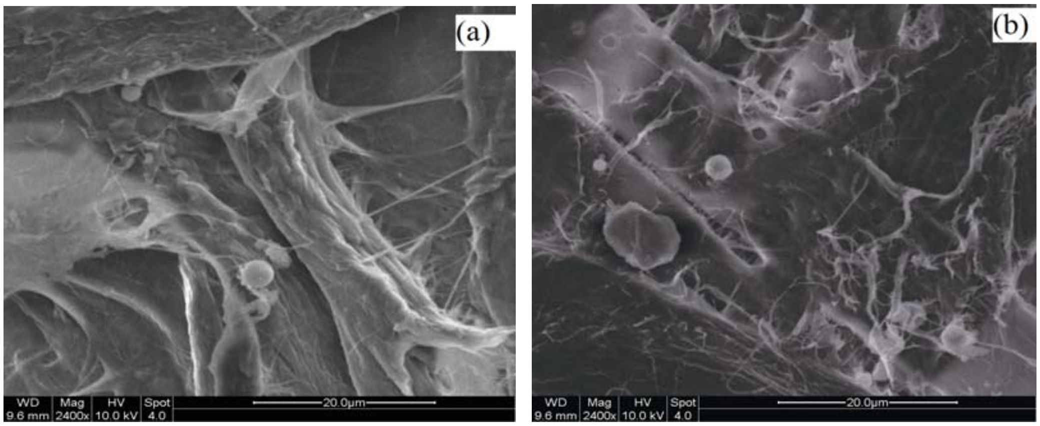

Fig. 5. SEM picture of paper with different beating degree, (a) pulp with 15000 revolutions, (b) pulp with 5000 revolutions

Based on the results shown above, it is reasonable to suppose that there must be a connection between the retention of RTM and the manner of beating. In order to prove this conclusion, a set of experiments was performed, and the results are given in Table 5. Under the condition of similar or the same beating degree, the chromatic aberration of pulp treated by high consistency refining was 9.7, however, the chromatic aberration of pulp treated by low consistency refining was only 8.2. Low consistency refining and high consistency refining played different roles in the beating of fiber. The former mainly contributed to the shortening of fiber, and fibrillation of fiber was the key action of high-consistency refining. This phenomenon further confirmed that fibrillation of fiber was favorable to the retention of RTM.

Table 5. Effect of the Manner of Beating on the Retention of RTM

Beating manner	Beating degree, ^{o}SR	L*	a*	b*	Chromatic aberration
Low consistency refining	46.0	90.6	5.78	-0.46	8.2
High consistency refining	45.8	90.2	6.92	-0.83	9.7

(2) Effect of pulp composition on the retention of RTM

In practice, hardwood pulp is a cost-effective solution to improve some performance and value of paper. So, pulp furnish for printing papers is usually made up of hardwood pulp and softwood pulp together. As shown in Fig. 6, the chromatic aberration increased gradually with increasing of hardwood content.

In order to understand this phenomenon thoroughly, fiber morphologies of pulp furnishes were analyzed. As shown in Table 6, lower fiber length and width were achieved to a certain extent by increasing the content of hardwood pulp. However, fines content changed drastically, reaching as high as 48.52% when the furnish was hardwood pulp entirely. This indicated that the retention of RTM was closely related to the content of fines, which could contribute to larger a surface area of fiber and improved adsorption of RTM.

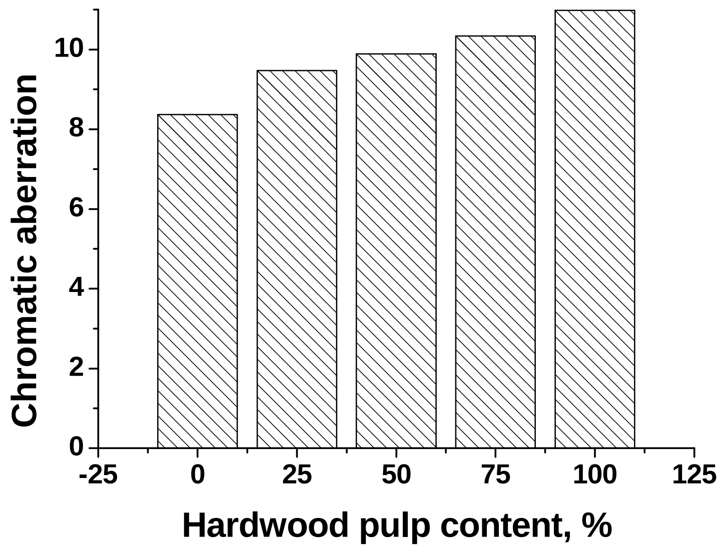

Fig. 6. Chromatic aberration of paper with different hardwood content

Table 6. Fiber Morphology of Different Pulp Furnish

Hardwood pulp content, %	Fiber Mean length, mm			Width, μm	Fines content, %	
	Arithmetic length	Length weighted length	Weight weighted length		Arithmetic length	Length weighted
0	1.487	2.339	1.167	26.0	42.05	8.84
25	1.181	1.932	1.743	22.7	44.13	8.82
50	1.030	1.599	2.291	20.3	45.22	8.22
75	0.900	1.237	2.619	18.7	46.14	8.18
100	0.812	0.985	2.905	18.8	48.52	7.60

(3) Effect of chemicals on retention of RTM

Filler and retention aid are necessary ingredients for most paper, not only to improve the optical properties and printability of papers but also to reduce the cost (Liu and Ni 2008). So, effects of the filler and retention aid on retention of RTM were investigated.

PCC is widely used as a filler due to its high purity, brightness, light scattering coefficient, and bulk. Effect of PCC on chromatic aberration due to RTM is shown in Fig. 7. The curve in Fig. 7 indicates that chromatic aberration decreased dramatically in the presence of PCC, especially when PCC dosage increased from 0 to 20%, but there was little further change when PCC dosage was increased above the 20% level.

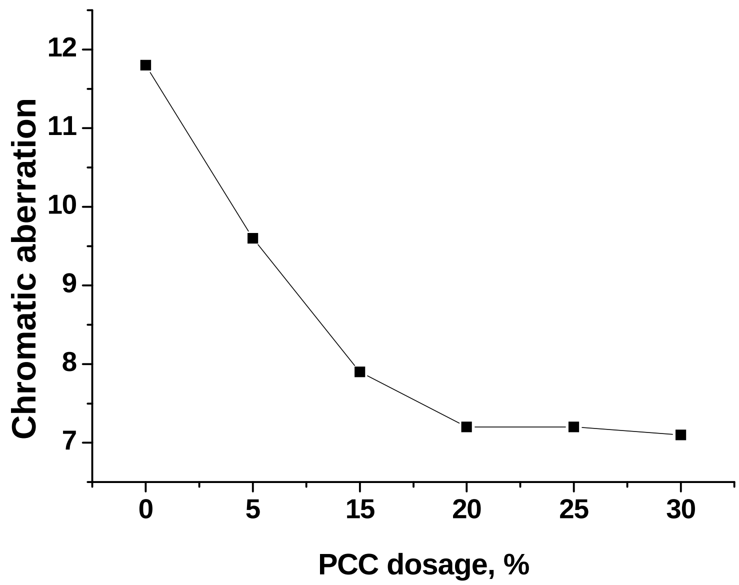

Fig. 7. Effect of PCC dosage on retention of RTM (adding PCC prior to RTM)

Different addition orders of PCC and RTM also affected the retention of RTM, as shown in Fig. 8. Considering the retention of RTM, RTM should have priority over PCC to be added. It's well known that the loss of fillers can reach as high as 50% in the wire section during papermaking. If the PCC was added first, it tended to adsorb more RTM than fibers due to its higher surface area. Thus, much of the RTM was wasted with the unretained portion of PCC. Conversely, when the RTM was adsorbed first by fibers, the chance of losing them with unretained PCC was reduced.

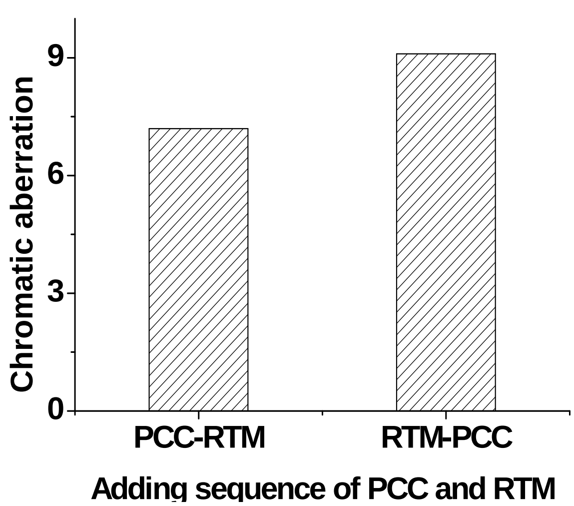

Fig. 8. Effect of PCC and RTM adding sequence on the retention of RTM (PCC dosage: 20%, RTM dosage: 0.6%)

Retention of fines and filler in the wet end can be increased by retention aids. RTM could be considered as a kind of microparticle due to its size and shape; thus its retention behavior in pulp might be correlated with the use of retention aids to a certain degree. CPAM is widely used as a retention aid in the wet end due to its high efficiency and low price. Its effect on chromatic aberration of paper was investigated, and the results are shown in Table 7. Chromatic aberration of paper increased with increasing the dosage of CPAM; however, when the dosage of CPAM was higher than 0.02%, chromatic aberration changed little on the whole. So, the optimal CPAM dosage should be 0.02% with respect to cost.

Table 7. Effect of CPAM Dosage on Retention of RTM

CPAM dosage/%	0	0.01	0.02	0.04	0.06	0.08
L*	88.26	84.10	82.92	82.65	82.21	81.96
a*	8.43	11.54	14.87	15.34	15.76	16.12
b*	-1.98	-2.87	-3.12	-3.24	-3.35	-3.41
Chromatic aberration	10.2	15.2	17.3	17.7	18.0	18.2

Effects of different addition sequences between RTM and CPAM on chromatic aberration are shown in Table 8. At a given dosage of CPAM, higher chromatic aberration could be achieved when RTM was added ahead of CPAM. If CPAM was added prior to RTM, the adsorption sites of CPAM were mainly occupied by fines and filler, thus, the RTM had less chance to act with CPAM and the retention of RTM was decreased greatly.

Table 8. Effect of Addition Sequence of RTM and CPAM on Retention of RTM

CPAM dosage/%	0.01		0.02	
Adding sequence	RTM-CPAM	CPAM-RTM	RTM-CPAM	CPAM-RTM
L*	85.62	87.13	83.14	86.03
a*	10.47	9.16	11.68	10.31
b*	-2.63	-2.17	-3.10	-2.54
Chromatic aberration	14.8	12.1	16.7	14.4

CONCLUSIONS

1. The reversible themochromic microcapsules exhibited strong color contrast between cool and heated conditions, and this effect was considered to be suitable for use in the preparation of anticounterfeiting paper.
2. The surface of microcapsules was smooth, and there was no adhesion between particles. The diameters of microcapsules were mainly in the range of 3.0 μm to 5.0 μm.

3. Retention of RTM was closely related to the beating degree and pulp composition; the higher the beating degree and hardwood pulp content, the higher the retention of RTM. On the other hand, retention of RTM was influenced by filler and retention aid. Retention aid addition could promote the retention of RTM to someextent. However, filler was not conducive to the retention of RTM. Different addition sequences between RTM and filler or retention aid also influenced the retention of RTM.

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