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Influence of Thermochromic Pigment Powder on Properties of Waterborne Primer Film for Chinese Fir

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Abstract: This study chose organic thermochromic pigment powder and waterborne wood primer as the paint base, and Chinese fir board as the substrate to prepare thermochromic waterborne coatings with different concentrations of thermochromic pigment powder. The best concentration of thermochromic pigment powder for waterborne primer film on Chinese fir surface was explored. The experimental results showed that the color-changing property of the primer film was the best when the concentration of pigment powder in primer film was 5.0%–10%. There was a negative correlation between the gloss of the primer and the concentration of pigment powder. The gloss of the primer film was the highest when the concentration of pigment powder was 5%. When the concentration of pigment powder is 0%–20% and 25.0%–30%, the adhesion of the coating is grade 0 and grade 1, respectively. The resistance to the impact of primer film increased with the increase of concentration of pigment powder, but the resistance to the impact of primer film with 0%–30% of thermochromic pigment powder concentration was similar. Scanning electron microscopy showed that the higher the concentration of thermochromic pigment powder, the more particles and agglomeration. When the concentration of pigment powder was 5%, the distribution of particles was uniform and no agglomeration, and the microstructure of primer film was the best. Infrared spectroscopy showed that there was no difference in the composition of the paint film from 0% to 30%. The results showed that the comprehensive property of waterborne primer film on Chinese fir was better when the pigment concentration was 5%. Waterborne thermochromic primer film provides a potential application for the development of intelligent furniture in different temperature ranges.

Keywords: thermochromic pigment powder; waterborne wood primer; performance

1. Introduction

Thermochromic materials refer to unique materials whose color will change when a class of compounds or mixtures are heated or cooled [1]. From the thermodynamic point of view, thermochromic materials can be classified as irreversible thermochromic materials and reversible thermochromic materials [2]. Similarly, thermochromic materials mainly include three categories: inorganic, organic, and liquid crystal materials in terms of their properties and composition [3]. In a certain sense, the organic thermochromic powder is the product of microencapsulation with the organic thermochromic material as the core material [4]. Microencapsulation can isolate the discolored material from the external environment and improve its stability by controlling the core and wall material [5]. In certain solvents, the color is changed by the electron movement between the leuco agent (electron donor) and the chromogenic reagent (electron acceptor) when the temperature rises or falls [6]. Compared with other inorganic and liquid crystal color-changing systems, the organic color-changing system has many advantages, such as free color selection, reversibility of discoloration, low discoloration temperature, long life and high sensitivity [7].

At present, thermochromic color-changing materials are widely used in construction, textile, anti-counterfeiting and other fields. Xu et al. [8] designed and successfully prepared a VO_2 film featuring a "removable" anti-reflective coating, which opened up a new way for the application of low-cost intelligent windows. Wang et al. [9] prepared a poly-(3,4-ethylenedioxythiophene) (PEDOT) coating on hydrophobic polypropylene nonwoven fabric using mussel-like tannin-iron as the modified coating. This is a crucial step towards the realization of functional textiles. Liu et al. [10] obtained the organic thermochromic phase change system by mixing fluorinated dyes, bisphenol A and aliphatic alcohol based on different ratios. This research showed great application prospects of anti-counterfeiting and fabricated thermally-responsive photonic crystal successfully.

Chinese fir is widely used in buildings, bridges, furniture, wood products and other fields [11] because of its excellent properties, such as light material, easy processing, difficult deformation, insect resistance and corrosion resistance [12]. The waterborne wood coating uses water as the solvent, which has little harm to human body and environment in the process of production, construction and use, and has many advantages, such as flame-retardant, stable performance, good flexibility, oil energy saving and good adhesion strength [13,14]. However, there are still some development drawbacks in the use of waterborne coatings, such as high gloss [15], poor impact resistance [16], no thermochromic reaction, etc. Organic thermochromic pigment powder, which is added to waterborne coatings and applied to the wood surface, can maintain its original properties and achieve beautiful discoloration when the temperature changes. The waterborne primer contains about 90% of waterborne organic materials. In the process of wood finishing, the primary function of waterborne primer is to cooperate with the process of filling vessels and dyeing. For example, the primer can enhance the binding force with the vessels and prevent the coating from falling off, from facilitating the sequence of later processes. However, there are few reports about thermochromic color-changing waterborne primer coatings on wood materials.

In this paper, the waterborne wood primer was used as the paint base, the Chinese fir board was used as the substrate, and the red to yellow organic thermochromic pigment powder was added to the waterborne primer to prepare the thermochromic color-changing waterborne coatings to be applied on the wood surface. Specifically, in this experiment, the bisphenol A and methyl red were encapsulated in microcapsules, by using the bisphenol A and methyl red as the core material and melamine as the wall material. The aim of the study was to evaluate the optical properties, mechanical properties, liquid resistance, scanning electron microscopy and infrared spectroscopy of the primer film.

2. Materials and Methods

2.1. Test Materials

Electron transfer type organic thermochromic pigment powder, in the form of microcapsules, was composed of methyl red, bisphenol A, and melamine. The details of the experimental materials are shown in Table 1. The waterborne wood primer was composed of waterborne acrylic resin (the concentration was 70%), waterborne polyurethane resin (the concentration was 20%), titanium dioxide (the concentration was 5%), dipropylene glycol butyl ether (the concentration was 1%), propanediol butyl ether (the concentration was 2%) and ethylene glycol butyl ether (the concentration was 2%). The solid concentration of the coating is about 30%. Chinese fir boards (100 mm × 100 mm × 12 mm) were provided by Yihua Lifestyle Technology Co., Ltd., Shantou, China.

Table 1. Experimental materials.

Compound	Molecular Formula	M_W (g/mol)	CAS No.	Producer	Concentration (%)	Function
methyl red	$C_{15}H_{15}N_3O_2$	269.30	493-52-7	Huancai Discoloration Technology Co., Ltd., Shenzhen, China	99.9	leuco agent
bisphenol A	$C_{15}H_{16}O_2$	228.29	80-05-7	Huancai Discoloration Technology Co., Ltd., Shenzhen, China	99.9	chromogenic reagent
melamine	$C_3H_6N_6$	126.12	108-78-1	Huancai Discoloration Technology Co., Ltd., Shenzhen, China	99.9	wall material
sodium dodecylbenzene sulfonate	$C_{18}H_{29}NaO_3S$	348.48	25155-30-0	Xilong Chemical Co., Ltd., Guangzhou, China	99.9	emulsifier
formaldehyde solution	CH_2O	30.03	50-00-0	Xilong Chemical Co., Ltd., Guangzhou, China	37.0	wall material
anhydrous ethanol	C_2H_6O	46.07	64-17-5	Xilong Chemical Co., Ltd., Guangzhou, China	99.9	for rinsing microcapsules
lauryl alcohol	$C_{12}H_{26}O$	186.34	112-53-8	Xilong Chemical Co., Ltd., Guangzhou, China	99.9	co-solvent
citric acid monohydrate	$C_6H_{10}O_8$	210.14	5949-29-1	Xilong Chemical Co., Ltd., Guangzhou, China	99.9	pH regulator
triethanolamine	$C_6H_{15}NO_3$	149.19	102-71-6	Xilong Chemical Co., Ltd., Guangzhou, China	99.9	pH regulator
NaCl solution	–	–	–	Qingdao Hainuo Bioengineering Co., Ltd., Qingdao, China	15.0	liquid resistance test solution
medical ethanol	–	–	–	Qingdao Hainuo Bioengineering Co., Ltd., Qingdao, China	70.0	liquid resistance test solution
detergent	–	–	–	Shanghai Hutchison Whitecat Co., Ltd., Shanghai, China	–	liquid resistance test solution
red ink	–	–	–	Fine Stationery Co., Ltd., Shanghai, China	–	liquid resistance test solution
waterborne wood primer	–	–	–	Hengchang paint Co., Ltd., Huiyang, China	–	primer film

M_W = Molecular Weight.

2.2. Preparation of Thermochromic Pigment Powder

The preparation method of thermochromic pigment powder was in-situ polymerization. The 10.0 g melamine and 20.0 g 37% formaldehyde solution was mixed and stirred, dissolved to obtain the milky white solution, and then 20.0 mL deionized water was added. The value of pH was adjusted to 8.4–8.8 by triethanolamine. Afterwards, the solution was kept at 70 °C in the constant temperature water bath, the stirring speed was 700 rpm, the stirring time was 1 h, and the transparent solution (A) was obtained. Two grams of sodium dodecylbenzene sulfonate was entirely dissolved in 198.00 g deionized water to get 1% sodium dodecylbenzene sulfonate aqueous solution. Then 2.0 g methyl red, 2.0 g bisphenol A, and 20.0 g lauryl alcohol were added into the aqueous sodium dodecylbenzene sulfonate solution, and the beaker was placed in 60 °C water bath, stirred for 45 min at 1200 rpm to produce a stable emulsion (B). Then the A solution was dropped to the B emulsion by the suction tube, mixed evenly. Citric acid monohydrate was prepared into the aqueous solution and then dripped into the emulsion with the aim of adjusting pH to 4.5–5.2. The whole system was kept reacting at 60 °C for 3 h and cooled to room temperature. The product was rinsed with deionized water and anhydrous ethanol for many times and dried in a freeze-drying machine for 120 h to obtain 12.0 g of thermochromic pigment powder.

2.3. Preparation of Thermochromic Color-Changing Waterborne Coatings

The thermochromic pigment powder was added into the waterborne wood primer, and thermochromic color-changing waterborne coatings with the concentration of 0%, 5%, 10%, 15%, 20%, 25% and 30% were respectively prepared (Table 2). After stirring evenly, the mixture was applied on Chinese fir board with SZQ tetrahedral fabricator (Tianjin Jinghai science and technology testing machinery factory, Tianjin, China). After the surface was dried for about 30 min, all samples were transferred to an electric blast drying oven at 35 °C to heat them until the mass of the samples no longer changed, then taken out and cooled to room temperature naturally. The primer film was polished gently by 1000 mesh sandpaper after it was dry, and the dust was wiped off. The above process was repeated three times. The thickness of the prepared dry primer film was 60 µm approximately.

Table 2. Composition of thermochromic color-changing waterborne coatings.

Thermochromic Pigment Powder Concentration (%)	Thermochromic Color-Changing Powder (g)	Waterborne Primer (g)	Thermoreversible Color-Changing Waterborne Coatings (g)
0	0	100.0	100.0
5.0	5.0	95.0	100.0
10.0	10.0	90.0	100.0
15.0	15.0	75.0	100.0
20.0	20.0	80.0	100.0
25.0	25.0	75.0	100.0
30.0	30.0	70.0	100.0

2.4. Performance Test

The microstructure of waterborne primer was analyzed by Quanta 200 environment scanning electron microscope (SEM) and FEI company (Hillsboro, OR, USA). The composition of waterborne primer film was analyzed by vertex 80V infrared spectrum analyzer (Germany Bruker Co., Ltd., Karlsruhe, Germany). CIELAB values of waterborne primer film were determined by the HP-2136 colorimeter (Zhuhai Tianchuang Instrument Co., Ltd., Zhuhai, China). The gloss of waterborne primer film was measured by the HG268 gloss meter (Shenzhen 3nh Technology Co., Ltd., Shenzhen, China). On the basis of GB/T 1732-1993 [17], the resistance to the impact was measured by the QCJ impactor (Tianjin Jingkelian Material Testing Machine Co., Ltd., Tianjin, China). The primer film surface shall be placed on the iron paste face up, and the 1.0 kg heavy hammer shall be fixed on a certain height of the sliding cylinder (the maximum height is 50.0 cm) by the control device. The control button was pressed, and the heavy hammer shall fall freely on the primer sample plate. After the test, the heavy hammer was lifted, and the test plate was taken out. The deformation of the film was observed. If the primer film does not crack, the maximum drop height of the ball is the impact resistance value. On the basis of GB/T 1720-1989 [18], the adhesion of the primer film was determined by QFZ-II coating adhesion tester (Tianjin JingKelian Material Testing Machine Co., Ltd., Tianjin, China). The hardness of film was measured with 6H-6B pencil. In this experiment, the Chinese fir board was fixed on the horizontal table, the angle between the fixed pencil and the primer film was 45°, and the hardness of film was measured under the load of 1.0 kg. When there were scratches on the primer film, the hardness of the film was measured. On the basis of GB/T 1733-1993 [19], the liquid resistance of the primer film was measured with 15% NaCl solution, 70% medical ethanol, detergent, and red ink. The filter paper was soaked in sodium chloride solution, medical ethanol, detergent or red ink, then placed on the top of Chinese fir board primer film, and finally covered with a glass cover for 24 h. All the experiments were repeated four times, and the error was less than 5%.

3. Results and Discussion

3.1. Influence of Thermochromic Pigment Powder on Optical Properties

The chromatic values of the paint film with different concentrations of pigment powder from 18 to 40 °C are shown in Table 3. L, a, b represent the change of bright and dark, red and green, and yellow and blue of the measured objects, respectively. c is the color saturation. H is the hue. The difference values ΔL, Δa, Δb, respectively, are represented as the white-black, red-green, and yellow-blue color difference. Then the color difference (ΔE) was calculated on the basis of formula (1):

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

It can be seen from Table 3 that when the temperature is 18 °C, the bright-dark value of the primer film without thermochromic pigment powder is 85.5, red-green value is 6.1, the yellow-blue value is 29.5, the color saturation is 30.1, and the hue is 78.1. The chromatic values of primer film containing 5.0%–10% thermochromic pigment powder changed significantly at 32 °C.

Figure 1 was drawn according to the result of color difference. It can be seen from Figure 1 that the color difference of the primer film without thermochromic pigment powder was 0.8–1.0 within the range of temperature change, and it was basically unchanged. When the heating temperature was 30 °C, the color difference of the primer film with 5% pigment powder was 5.4. When the heating temperature was 32 °C, the color difference of the primer film with 5% pigment powder was 106.0. The color difference of primer film containing 10% thermochromic pigment powder changed significantly at 32 °C, which increased to 110.5. However, when the heating temperature was 32 °C and the pigment powder concentration of the primer film was more than 10%, the color difference did not change significantly. It can be concluded that the film had a better discoloration influence under the circumstances of adding 5.0%–10% pigment powder.

Table 3. Influence of thermochromic pigment powder on the color variation of the waterborne primer film.

Thermochromic Pigment Powder Concentration (%)	Chromatic Values	18 °C	20 °C	22 °C	24 °C	26 °C	28 °C	30 °C	32 °C	34 °C	36 °C	38 °C	40 °C
	L	85.5	85.2	84.8	85.0	85.1	85.3	84.7	84.7	84.6	84.7	84.7	84.7
	a	6.1	5.4	6.3	6.5	6.6	5.9	6.1	5.9	5.0	5.6	5.9	6.3
0	*b*	29.5	29.5	29.9	30.1	29.7	30.3	29.5	29.8	29.9	29.7	29.8	29.5
	c	30.1	30.0	30.6	30.8	30.4	30.9	30.1	30.3	30.3	30.2	30.3	30.2
	H	78.1	79.5	78.0	77.8	77.4	78.8	78.2	78.8	80.4	79.3	78.8	77.9
	L	52.2	52.9	51.6	52.0	53.9	52.3	54.5	95.4	97.7	97.0	97.4	97.5
	a	60.8	60.2	61.3	61.6	57.9	60.4	56.1	−21.9	−23.3	−22.2	−22.7	−23.1
5	*b*	42.7	42.4	41.2	42.3	44.1	42.0	43.9	92.9	97.7	93.8	96.1	96.5
	c	74.3	73.6	73.8	74.8	72.8	73.6	71.3	95.5	100.5	96.4	98.7	99.3
	H	35.0	35.1	33.9	34.4	37.2	34.8	38.0	103.2	103.4	103.3	103.3	103.4
	L	49.4	49.9	49.8	49.7	49.6	50.0	50.3	94.8	99.4	99.5	100.0	100.0
	a	60.3	59.5	60.3	59.7	59.4	59.8	59.7	−14.2	−22.4	−22.9	−23.9	−24.4
10	*b*	36.2	36.3	37.1	36.8	36.6	36.5	37.3	104.0	113.1	113.6	115.0	114.6
	c	70.3	69.7	70.8	70.2	69.8	70.1	70.4	105.0	115.3	115.9	117.5	117.2
	H	31.0	31.4	31.6	31.6	31.7	31.4	32.0	97.7	101.1	101.4	101.7	102.0
	L	50.1	50.2	49.9	49.8	49.6	49.8	49.0	49.9	91.7	98.7	96.9	97.1
	a	57.2	56.8	57.9	57.7	58.0	57.3	55.7	53.7	−1.9	−16.6	−17.9	−18.2
15	*b*	34.2	33.6	33.6	33.5	34.0	34.5	32.8	34.2	99.3	115.6	110.5	111.4
	c	66.6	66.0	67.0	66.8	67.2	66.9	64.7	63.7	99.3	116.8	111.9	112.9
	H	30.8	30.6	30.1	30.1	30.4	31.0	30.5	32.4	91.1	98.2	99.2	99.3
	L	50.6	51.2	50.0	50.8	49.9	50.0	50.1	50.3	64.7	95.3	98.1	98.7
	a	56.3	55.8	55.8	54.1	56.1	55.0	55.2	55.1	41.5	−7.8	−13.9	−15.2
20	*b*	32.8	34.2	33.2	33.4	32.1	32.5	32.6	32.2	47.9	104.8	112.7	113.4
	c	65.1	65.5	64.9	63.6	64.6	63.9	64.1	63.9	63.4	105.0	113.6	114.5
	H	30.2	31.5	30.7	31.7	29.8	30.5	30.5	30.3	49.1	94.2	97.0	97.6
	L	50.8	50.5	49.2	50.5	49.4	49.2	49.6	56.4	95.7	96.9	96.5	96.8
	a	53.6	53.4	52.9	51.9	53.7	52.9	53.0	46.4	−10.3	−11.9	−13.2	−12.7
25	*b*	31.8	32.0	30.6	32.1	31.0	30.6	31.5	38.7	107.6	109.8	109.9	110.1
	c	62.3	62.3	61.2	61.1	62.0	61.2	61.7	60.4	108.1	110.4	110.7	110.9
	H	30.6	30.9	30.0	31.7	30.0	30.0	30.7	39.8	95.4	96.2	96.8	96.6
	L	50.4	50.7	49.4	50.2	49.2	49.6	49.5	49.1	79.4	93.0	94.8	95.1
	a	52.8	51.5	52.7	49.2	51.6	52.0	51.8	50.1	14.7	−7.8	−9.8	−10.1
30	*b*	31.7	31.6	30.2	31.7	30.9	30.7	30.6	29.9	74.9	102.6	105.9	106.8
	c	61.6	60.5	60.8	58.6	60.1	60.4	60.2	58.4	76.4	102.9	106.3	107.3
	H	30.9	31.5	29.8	32.7	30.9	30.6	30.6	30.8	78.8	94.3	95.3	95.4

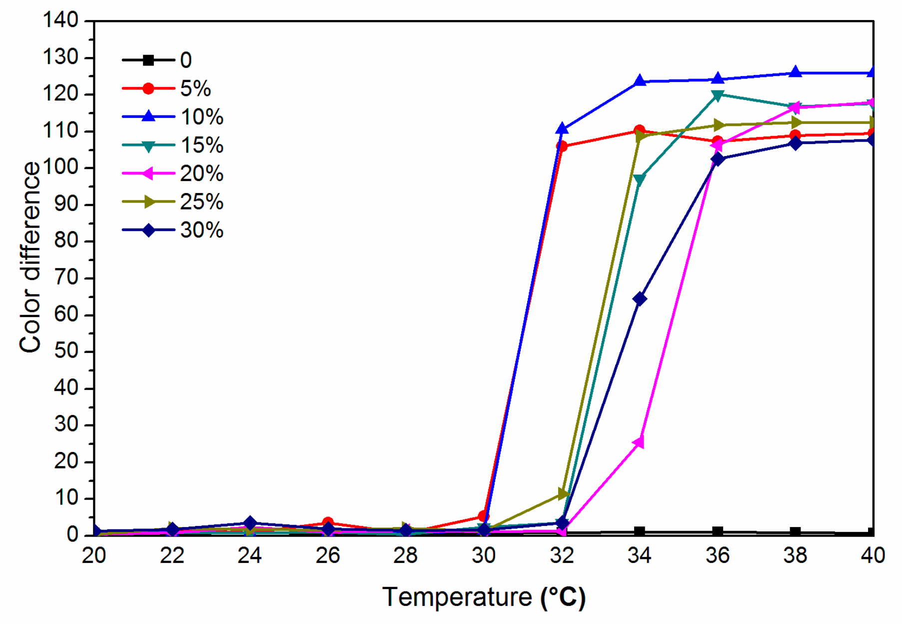

Figure 1. The effect of concentration of thermochromic pigment powder on color difference of waterborne primer film from 18 to 40 °C.

To ensure the same incident light intensity, different incident angles (20°, 60°, and 85°) of light were used to irradiate the primer film added with the thermochromic pigment powder. The influence of the concentration of pigment powder on the gloss of film is shown in Table 4. At the same incident angle, the gloss of the primer is negatively related to the concentration of pigment powder. This is due to the increase of the concentration of the color changing pigment powder, which resulted in the increase of particles and the decrease of the reflection of the light on the primer film [20]. When adding thermochromic pigment powder concentration was the same, the gloss of the primer film is positively related to the incident angle. The gloss of the primer film was higher under the circumstances of adding 5% pigment powder.

Table 4. Influence of different concentrations of the color-changing powder on the gloss of the primer film at 20°, 60°, and 85°.

Thermochromic Pigment Powder Concentration (%)	20° (%)	60° (%)	85° (%)
0	12.2 ± 0.4	45.5 ± 0.9	52.5 ± 0.4
5.0	2.4 ± 0.1	12.4 ± 0.3	26.9 ± 0.4
10.0	1.1 ± 0	6.8 ± 0.1	13.5 ± 0.1
15.0	0.7 ± 0	3.7 ± 0.1	9.2 ± 0.1
20.0	0.4 ± 0	2.4 ± 0.1	9.4 ± 0.1
25.0	0.3 ± 0	1.5 ± 0	8.0 ± 0.2
30.0	0.3 ± 0	1.4 ± 0	7.8 ± 0.1

3.2. Influence of Thermochromic Pigment Powder on Mechanical Properties

It can be seen from Table 5 that with the concentration of pigment powder increasing, the adhesion of the primer film with 0%–20% concentration of thermochromic pigment powder was excellent, and the adhesion grade was grade 0. After the adhesion test, the damaged area of the primer film with 25% and 30% concentration of thermochromic pigment powder increased to 5% and the adhesion decreased to grade 1. Due to the high concentration of thermochromic pigment powder, the proportion of waterborne solvent in the waterborne coating decreased, which affected the adhesion between the primer film and Chinese fir, resulting in the decrease of the adhesion of the primer film [21]. As shown in Table 6, the resistance to the impact of the primer film was positively correlated with the concentration of pigment powder. This is because when the thermochromic pigment powder particles increase, it plays a positive role in the stress transfer between the particles and the substrate, making the load capacity become stronger [22]. However, the wood density was positively correlated with its mechanical strength. The density of Chinese fir was lower than 0.4 kg/m^3, and its impact resistance was low [23]. Therefore, the impact resistance of primer film with 0%–30% pigment powder was not high, and there was little difference.

Table 5. Influence of different concentrations of the thermochromic pigment powder on the adhesion of the primer film.

Thermochromic Pigment Powder Concentration (%)	Damaged Area (%)	Adhesion Grade
0	0 ± 0	0 ± 0
5.0	0 ± 0	0 ± 0
10.0	0 ± 0	0 ± 0
15.0	0 ± 0	0 ± 0
20.0	0 ± 0	0 ± 0
25.0	5 ± 0	1 ± 0
30.0	5 ± 0	1 ± 0

Table 6. Influence of different concentrations of the thermochromic pigment powder on the resistance to the impact of the primer film.

Thermochromic Pigment Powder Concentration (%)	Resistance to the Impact (kg·cm)
0	5.0
5.0	5.0
10.0	6.0
15.0	7.0
20.0	7.0
25.0	7.0
30.0	9.0

3.3. Influence of Thermochromic Pigment Powder on Liquid Resistance Properties

For the primer film containing 0%–30% concentration of pigment powder, the liquid resistance test with four kinds of the solution was carried out. The chromatic values of the primer film were measured 24 h before and after the test at room temperature of 18 °C (Table 7). The color difference was calculated and analyzed, and the results were shown in Table 8. According to liquid resistance grade (Table 9) and the test results (Figure 2), the liquid resistance of primer film with different concentrations of pigment powder to NaCl solution, medical ethanol, and detergent was grade 1, and there was no obvious trace. However, the resistance of red ink was grade 3, with obvious discoloration. Therefore, the concentration of thermochromic pigment powder had little influence on the liquid resistance of the coating.

Table 7. Influence of different concentrations of the thermochromic pigment powder on the color variation of the primer paint film.

Thermochromic Pigment Powder Concentration (%)	Chromatic Values	Original	NaCl	Detergent	Ethanol	Red Ink
0	*L*	85.5	85.7	86.2	86.1	73.4
	a	6.1	6.3	6.8	6.2	40.2
	b	29.5	30.3	30.2	30.5	19.6
	c	30.1	31.1	31.0	31.2	44.8
	H	78.1	77.0	77.5	78.6	26.0
5	*L*	52.2	52.5	52.8	53.1	55.9
	a	60.8	59.8	61.1	60.7	57.4
	b	42.7	43.1	42.9	43.1	41.4
	c	74.3	73.8	75.5	74.0	70.8
	H	35.0	36.4	34.6	35.6	35.8
10	*L*	49.4	50.1	50.9	49.6	47.7
	a	60.3	61.0	59.6	59.7	64.7
	b	36.2	36.1	36.8	36.0	34.9
	c	70.3	70.9	69.5	67.2	73.5
	H	31.0	30.6	31.9	30.4	28.3
15	*L*	50.1	49.7	49.9	49.5	48.8
	a	57.2	58.1	58.1	57.6	61.7
	b	34.2	33.9	33.7	34.3	32.6
	c	66.6	67.2	67.2	66.1	69.8
	H	30.8	29.7	30.1	29.3	27.8
20	*L*	50.6	50.2	50.8	49.8	48.4
	a	56.3	55.7	55.8	57.0	58.3
	b	32.8	31.9	32.3	32.6	30.3
	c	65.1	64.8	64.5	64.9	65.7
	H	30.2	29.6	30.0	29.2	27.4
25	*L*	50.8	50.8	50.9	50.3	48.7
	a	53.6	54.2	54.2	54.1	57.2
	b	31.8	31.5	31.7	30.9	29.2
	c	62.3	63.3	63.7	62.8	64.2
	H	30.6	29.9	29.8	29.2	27.0
30	*L*	50.4	50.5	50.4	49.7	48.7
	a	52.8	53.6	53.9	53.7	57.0
	b	31.7	31.1	31.8	30.9	29.1
	c	61.6	62.2	63.0	62.2	64.0
	H	30.9	30.0	29.2	28.8	27.0

Table 8. Influence of thermochromic pigment powder on the color difference of the waterborne primer film.

Thermochromic Pigment Powder Concentration (%)	NaCl	Detergent	Ethanol	Red Ink
0	0.8	1.2	1.2	37.5
5.0	1.1	0.7	1.0	5.2
10.0	1.0	1.8	0.7	4.9
15.0	1.0	1.0	0.7	4.9
20.0	1.2	0.7	1.1	3.9
25.0	0.7	0.6	1.1	4.9
30.0	1.0	1.1	1.4	5.2

Table 9. The liquid resistance grade of primer film with the different color-changing powder concentration.

Thermochromic Pigment Powder Concentration (%)	NaCl	Detergent	Ethanol	Red Ink
0	1	1	1	3
5.0	1	1	1	3
10.0	1	1	1	3
15.0	1	1	1	3
20.0	1	1	1	3
25.0	1	1	1	3
30.0	1	1	1	3

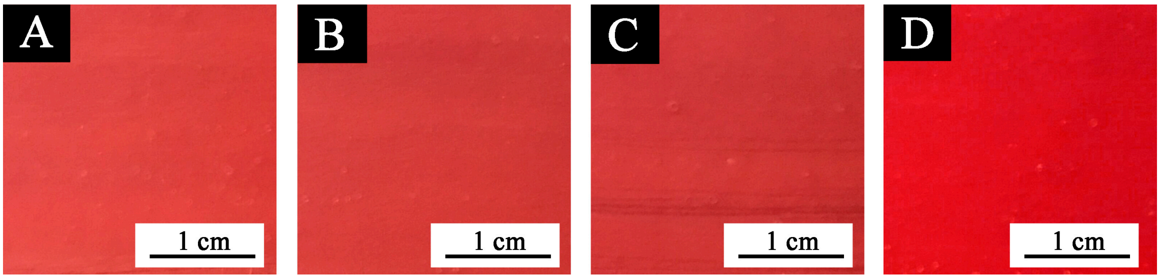

Figure 2. Images of coatings with 10% thermochromic pigment powder after liquid resistance test: (**A**) NaCl, (**B**) detergent, (**C**) ethanol, and (**D**) red ink.

3.4. The SEM Analysis of Thermochromic Color-Changing Waterborne Primer Film

SEM images of waterborne primer film with different concentrations of thermochromic pigment powder are shown in Figure 3. It can be seen from Figure 3 that the pure primer (Figure 3A) is smooth, with almost no particles. The particle size of the thermochromic pigment powder was approximately 6–8 μm (Figure 3B). The primer film of 5% pigment powder (Figure 3C) had obvious particles with uniform particle distribution without agglomeration. When the concentration of pigment powder increased to 10%, the particles increased and agglomerated obviously. The primer film with 30% thermochromic pigment powder (Figure 3E) had obvious agglomeration. Therefore, the agglomeration of primer film was positively correlated with the concentration of pigment powder. The microstructure of the primer film added 5% concentration pigment powder was better. The number of particles increased with the pigment powder concentration increasing, which leads to the decrease of the reflection of the film surface to the light; therefore, the gloss dropped greatly.

3.5. The Fourier Transform Infrared Spectroscopy (FTIR) Analysis of Thermochromic Color-Changing Waterborne Primer Film

The chemical composition of different concentrations of Chinese fir, thermochromic pigment powder, pure primer film and thermochromic waterborne primer film was measured by infrared spectroscopy, as shown in Figure 4. It can be seen from Figure 4 that bands at 3431 and 3343 cm^{-1} are the stretching vibration bands of –OH group. Bands at 2930, 2850 and 1445 cm^{-1} are the –CH_2 groups. The band at 1732 cm^{-1} is the C=O group with strong and sharp characteristics, which may be aldehyde or ketone. It can be seen from Figure 4 that there were absorption peaks representing C=C–H near 810 cm^{-1}, and the C–O stretching vibration band and the C–C skeleton stretching vibration absorption at 1150 cm^{-1} [24]. When the pigment powder was added to the primer, all peaks were not disappeared apart from –OH group, which basically did not affect the discoloration effect of the pigment powder, and still had the discoloration ability.

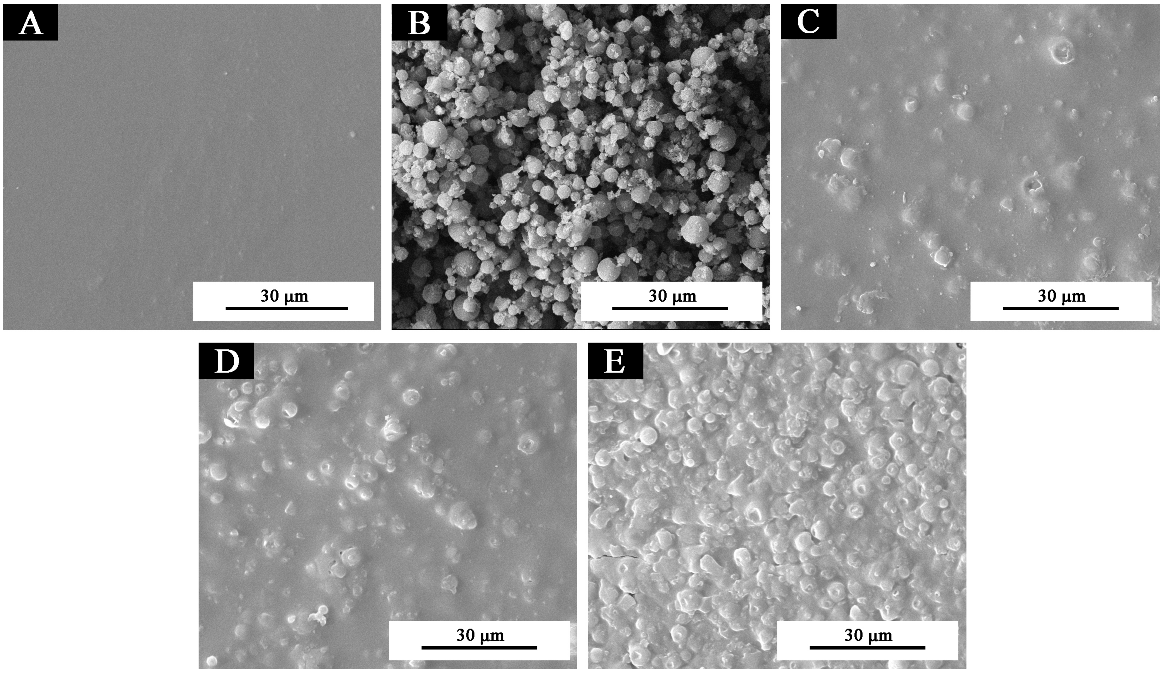

Figure 3. SEM of different concentrations of thermochromic pigment powder in the waterborne primer: (**A**) pure waterborne primer film; (**B**) thermochromic pigment powder; (**C**–**E**) 5%, 10% and 30% thermochromic pigment powder in the waterborne primer, respectively.

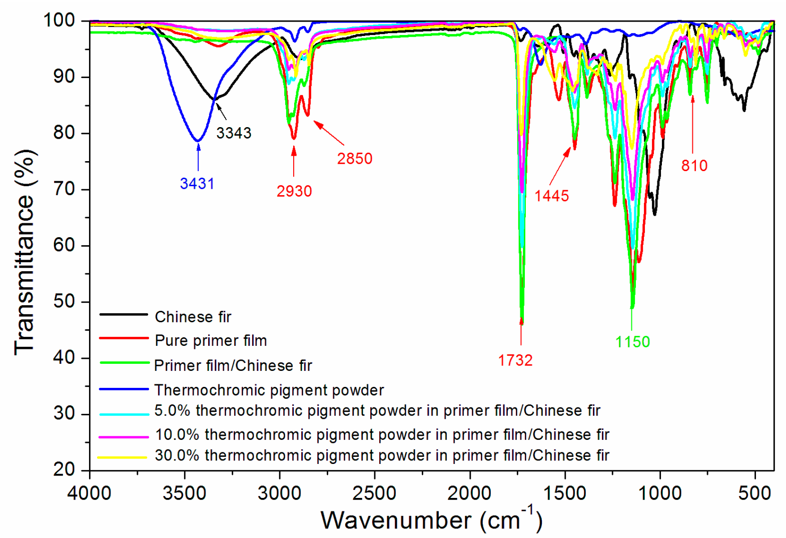

Figure 4. FTIR of different concentrations of thermochromic pigment powder in the waterborne primer film.

4. Conclusions

When the added thermochromic pigment powder concentration was 5% and 10%, the discoloration performance of the film was better. The gloss of the primer film decreased with increasing the pigment powder concentration. The gloss of the primer film was the second-highest when added 5% pigment powder. The adhesion of primer film added 0%–20% pigment powder was grade 0, and the adhesion of primer film with 25% and 30% pigment powder was grade 1. With the concentration of the pigment powder increasing, the resistance to the impact of the primer film increased, but the concentration of 0%–30% had little difference. The results of SEM showed that the higher the concentration of pigment powder, the more the particles, and the more the agglomeration. When the concentration of pigment powder was 5%, the particle distribution was uniform without agglomeration, and the primer film microstructure was the better. In the infrared spectrum test, there was no difference in the composition of the primer film when the concentration of the pigment powder was 0%–30%. According to the above results, when added 5% pigment powder concentration, the general performance of waterborne primer film was the better. This paper offers a reference for improving thermochromic color-changing waterborne primer coatings.

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