Effect of Urea-Formaldehyde (UF) with Waterborne Emulsion Microcapsules on Properties of Waterborne Acrylic Coatings Based on Coating Process for American Lime

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Abstract: The purpose of this paper is to explore the effect of urea-formaldehyde (UF) with waterborne emulsion microcapsules on the optical, mechanical and aging resistance properties of waterborne coatings from the perspective of coating process. In this paper, the microcapsules were prepared with UF resin as the wall materials and waterborne emulsion as the core materials. Based on the coating process, the optical, mechanical and aging resistance properties of the waterborne acrylic coatings with microcapsules for American lime were tested. The good coating process is three layers of primer, two layers of topcoat, and adding microcapsules into primer. The results showed that the coating process had little effect on the color difference of the paint film with microcapsules, the gloss of the paint film prepared by the good coating process was basically not changed, and the mechanical properties of the paint film were good. At this time, the hardness grade of the paint film was 3H, the adhesion was grade 0, the impact resistance was 110.0 N·cm⁻², and the elongation at break was 29.7%. The microcapsules added to the primer had better liquid resistance than those added to the topcoat. The paint film had good stability and aging resistance, and could inhibit the generation of microcracks to a certain extent. The paint film prepared by the good coating process had better comprehensive performance. This work provides a technical reference for self-healing of the waterborne coatings on American lime.

Keywords: microcapsule; coating process; waterborne coatings; paint film properties

1. Introduction

Waterborne wood coating is a kind of green and environmentally friendly coating with water as the main solvent. Compared with the traditional solvent-based wood coatings, it has the advantages of non-toxic and environmental protection, no smell, little volatile matter, non-combustion and explosion, no yellowing and large painting area, which is more and more welcomed by the market [1–3]. However, due to the low molecular weight and a large number of hydrophilic groups, the mechanical properties of waterborne wood coatings decrease to some extent [4,5]. In addition, due to the change in environmental factors (temperature, humidity, light), insufficient toughness of the coatings, and poor self-adaptation, microcracks will occur inside the paint film, and even damage the overall structure of the paint film, thus affecting the service life of the paint film and woodwork [6–8]. Therefore, it is an urgent problem to improve the mechanical properties of the paint film and inhibit the generation of microcracks.
Microcapsule is a kind of “core-shell structure”. The shell materials are deposited on the surface of the healing agent, which successfully covers the healing agent and forms microcapsules after certain drying treatment [9]. When the matrix with microcapsules is affected by various external forces, the embedded microcapsules are destroyed, and the repairing agent flows to the cracks to repair the cracks [10]. Microcapsule technology has been widely used in construction, shipping, dyeing and coatings [11]. Li et al. [12] studied the encapsulation of linseed oil in graphene oxide shells and prepared the self-healing composite coatings on the steel surfaces. The results showed that the waterborne polyurethane composite coatings containing 10% microcapsules autonomously healed a scratch with 20 µm in width. Bao et al. [13] improved the corrosion and water resistance of waterborne polyacrylate coating through introducing benzotriazole @ zinc oxide microcapsules. Aruna et al. [14] used in situ interfacial polymerization method to prepare the lubricating oil-encapsulated urea-formaldehyde microcapsules, and found that electrodeposited Ni coating containing oil-encapsulated microcapsules exhibited improved tribological properties compared to plain nickel coating. Li et al. [15] prepared tung oil-loaded microcapsules with the protection of poly(urea-formaldehyde) shells by in situ polymerization method. The epoxy coatings have an excellent corrosion resistance performance and self-lubricating performance by incorporating tung oil-loaded microcapsules into epoxy. Siva et al. [16] synthesized urea formaldehyde (UF) microcapsules loaded with linseed oil and mercaptobenzothiazole as core materials by in situ emulsion polymerization. The UF microcapsules incorporated epoxy coating on mild steel was found to offer better corrosion protection and self-healing ability than the microcapsules-free epoxy coating. Hsieh et al. [17] synthesized two differently sized poly(urea-formaldehyde)-shelled microcapsules with the suspension of carbon nanoparticles as the core via in situ polymerization. The results demonstrated that the smaller microcapsules in Ag paste exhibited better restoration efficiency than the larger one from the tensile test, whereas an opposite result was obtained from the scratching test. These above results showed that the application of microcapsule technology can prolong the service life of coatings and even improve the performance of coatings.

UF resin has the advantages of good compactness and toughness, good wear resistance and surface hardness [18,19]. Waterborne acrylic resin is environmentally friendly, non-toxic, good at film-forming, has excellent color retention, and can be cured at room temperature. The waterborne acrylic resin, as the core material of the microcapsules, was added into waterborne acrylic coatings, which is equivalent to using a part of the coatings as a repair agent for secondary curing at room temperature. It is easy to operate and does not introduce heterogeneous materials to the interface, which has potential effect on improving the performance of coatings for good interface compatibility. The coating process directly affects the adhesion, hardness, impact resistance of the paint film [20–22].

In order to explore the best coating process of waterborne coatings with microcapsules, the optical, mechanical and aging resistance properties of waterborne coatings, adding UF with waterborne emulsion microcapsules were explored by changing the number of primers, the number of topcoats and the way of adding microcapsules. The microstructure and chemical composition before and after aging were analyzed to explore the mechanism of good aging resistance, which laid a technical foundation for self-healing waterborne coatings for wood materials.

2. Materials and Methods

2.1. Experimental Materials

The 37.0% formaldehyde solution (M<sub>w</sub>: 30.03 g/mol, CAS No.: 50-00-0) was supplied by Shandong Baiqian Chemical Co., Ltd., Shandong, China. The urea (M<sub>w</sub>: 60.06 g/mol, CAS No.: 57-13-6) and triethanolamine (M<sub>w</sub>: 149.18, CAS No.: 102-71-6) were supplied by Dezhou Runxin Experimental Instrument Co., Ltd., Dezhou, China. The waterborne coating was supplied by Dulux Paint Co., Ltd., Shanghai, China. The main components were waterborne acrylic emulsion, polyurethane emulsion, thickener, water, etc. Citric acid monohydrate (M<sub>w</sub>: 210.14 g/mol, CAS No.: 5949-29-1) was supplied
by Jinan Qiwei Chemical Co., Ltd., Jinan, China. Sodium dodecyl benzene sulfonate was supplied by Liaocheng Sophia Chemical Reagent Co., Ltd., Liaochoeng, China. American lime (100 × 65 × 4 mm, uniform material chroma, 300 pieces, after ordinary mechanical sanding) was supplied by Shanghai Zhendan Furniture Co., Ltd., Shanghai, China. The American lime was placed at room temperature (20 °C) and relative humidity of 50.0% ± 5.0% for 7 days, so that the moisture in the wood reached a state of equilibrium (14.9%). The 15.0% NaCl solution was supplied by Dongguan pinggen Experimental Equipment Co., Ltd., Dongguan, China. The 70.0% medical ethanol was supplied by Suzhou Kangying Biotechnology Co., Ltd., Suzhou, China. White cat detergent containing 25.0% fatty alcohol ethylene oxide and 75.0% water was supplied by Shanghai Hehuang White Cat Co., Ltd., Shanghai, China. Red ink was supplied by Deli Group Co., Ltd., Ningbo, China.

2.2. Experimental Method

(1) Preparation of microcapsules

Microcapsules were prepared by in situ polymerization. The 20.0 g urea and 27.0 g of 37.0% formaldehyde solution were mixed and stirred, then the triethanolamine was added to adjust the pH value to 9.0–9.5. The solution was stirred at 100 rpm for 90 min at 70 °C and to prepare a slightly viscous and transparent UF prepolymer solution. In this way, the wall material was obtained and cooled to room temperature (20 °C).

The 1.37 g of sodium dodecyl benzene sulfonate was weighed and put into 135.6 mL of distilled water and stirred evenly to prepare a 1.0% sodium dodecylbenzene sulfonate aqueous solution. Then, the 17.5 g of Dulux waterborne acrylic coatings was added and stirred at 70 °C for 30 min to obtain the core material emulsion (waterborne emulsion).

At the speed of 300 rpm, the wall material emulsion was slowly dripped into the core material emulsion, and citric acid monohydrate were added to adjust the pH to 2.5–3.0. Then the mixture system was slowly raised to 70 °C and stirred for 3 h. After 5 days, the mixture was filtered and washed with distilled water and ethanol. The remaining solids were dried for 4 h at 80 °C, and the obtained white powder was UF with waterborne emulsion microcapsules.

(2) Preparation of the paint film

The primer and topcoat in this test were Dulux waterborne acrylic coatings. The previous experimental results showed that the best content in primer and topcoat is 10.0% [23]. According to the common coating process, the number of primer and topcoat is set to 2 and 3, respectively. The microcapsules were added to the topcoat and primer, respectively. The coating process design of waterborne acrylic coatings with microcapsules was shown in Table 1, and the ingredients of samples corresponding to Table 1 were shown in Table 2. As shown in Figure 1, No. 1# sample was taken as an example. The 2.0 g microcapsules were added into 18.0 g waterborne primer and mixed evenly. The waterborne primer added with microcapsules was coated on the surface of American lime substrate with SZQ tetrahedral fabricator (Dongguan Huaguo Precision Instrument Co., Ltd., Dongguan, China). The paint film was dried at room temperature (20 °C) for 30 min, then polished with 800 mesh sandpaper. The primer was applied twice. The waterborne topcoat without microcapsules was coated twice according to the same steps. The coated American lime was moved to 35 °C oven, heated to no change in quality, and then taken out and naturally cooled to room temperature. No. 2–8# samples were coated according to the same procedure. The thickness of the dried paint film was approximately 60 µm with SZQ tetrahedral fabricator (Dongguan Huaguo Precision Instrument Co., Ltd., Dongguan, China).
Table 1. Experimental schedule of coating process of the waterborne acrylic coatings with microcapsules.

| Experiment Number | Times of Coated Primer | Times of Coated Topcoat | Microcapsule Adding Method |
|--------------------|------------------------|-------------------------|---------------------------|
| 1#                 | 2                      | 2                       | primer addition           |
| 2#                 | 2                      | 3                       | primer addition           |
| 3#                 | 3                      | 2                       | primer addition           |
| 4#                 | 3                      | 3                       | topcoat addition          |
| 5#                 | 2                      | 2                       | topcoat addition          |
| 6#                 | 2                      | 3                       | topcoat addition          |
| 7#                 | 3                      | 2                       | topcoat addition          |
| 8#                 | 3                      | 3                       | topcoat addition          |

Table 2. Ingredients of the waterborne acrylic coatings with microcapsules.

| Experiment Number | Microcapsule Weight (g) | Weight of Waterborne Primer (g) | Weight of Waterborne Topcoat (g) | Weight of Waterborne Coating (g) |
|-------------------|-------------------------|---------------------------------|---------------------------------|----------------------------------|
| 1–4#              | 2.0                     | 18.0                            | 20.0                            | 40.0                             |
| 5–8#              | 2.0                     | 20.0                            | 18.0                            | 40.0                             |

2.3. Testing and Characterization

The morphology and chemical composition of microcapsules were analyzed by Quanta 200 environment scanning electron microscopy (SEM) (FEI Company, Hillsboro, OR, USA) and VERTEX 80V Fourier Transform Infrared (FTIR) spectroscopy (Germany BRUKER Co., Ltd., Karlsruhe, Germany). SEGT-J portable color difference meter (Beijing Times Peak Technology Co., Ltd., Beijing, China) was used to test the color difference of the paint film. L, a and b represent the lightness, red-green, and yellow-blue value of the paint film, respectively. L1, a1, b1, c1 and H1 were the chromaticity values of one point on the paint film, while L2, a2, b2, c2 and H2 were the chromaticity values of another point. \( \Delta L = L_1 - L_2 \), \( \Delta a = a_1 - a_2 \) and \( \Delta b = b_1 - b_2 \). \( \Delta L, \Delta a \) and \( \Delta b \) are expressed as brightness difference, red green index difference and yellow blue index difference, respectively [24]. The color difference (\( \Delta E \)) was calculated by Equation (1)

\[
\Delta E = \left[ (\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2 \right]^{1/2}
\]

HG268 intelligent gloss meter (Tianjin Shunnuo Instrument Technology Co., Ltd., Tianjin, China) was used to test the gloss of the paint film, and the gloss of the paint film was recorded at the incident angle of 20\(^\circ\), 60\(^\circ\) and 85\(^\circ\) [25]. Pencil hardness tester and 6H-6B pencils (Dongguan Huaguo Precision Instrument Co., Ltd., Dongguan, China) were used to measure the hardness of the paint film. Different types of pencil with hardness from soft to hard were used to scratch the paint film, which were 6B, 5B, 4B, 3B, 2B, HB, B, 2H, 3H, 4H, 5H, 6H. The greater the number B, the softer the pencil. The greater the H, the harder the pencil. The pencil was inserted into the instrument, clamped with clamps, and kept level. The pencil tip was placed on the surface of the paint film and pushed forward for 7.0 mm at the speed of 0.5–1.0 mm/s. When the paint film was not damaged, the maximum hardness of the pencil was the hardness of the paint film [26]. The adhesion of the paint film was tested by QFH-HG600 film scratch tester (Shenzhen Yeguan Instrument Equipment Co., Ltd., Shenzhen, China). The blade was perpendicular to the surface of the
sample, and the film was cut at a uniform rate under uniform pressure. The 100 of 1 × 1 mm grids were drawn on the surface of the sample. All cuts shall be cut to the surface of the substrate. The adhesive tape was firmly adhered to ensure good contact between the paint film and the adhesive tape, and then torn off at 60° angle. The damage of the paint film was observed with a magnifying glass to determine the adhesion grade of the paint film [27]. The adhesion grades of paint film can be divided into 0, 1, 2, 3, 4 and 5 grades from superior to inferior. Grade 0 indicated that the paint film surface had not fallen off. Grade 1 indicated that about 5% of the paint film surface had fallen off. Grade 2 indicated that the paint film surface has fallen off by 15%. Grade 3 indicated that 35% of the paint film had fallen off. Grade 4 indicated that the paint film surface had fallen off by about 55%. Grade 5 indicated that the paint film surface had fallen off seriously, exceeding 60%. The impact resistance of the paint film was tested by QCJ impactor tester (Tianjin Shunnuo Instrument Technology Co., Ltd., Tianjin, China) according to GB/T 1732-1993 [28]. The 1.0 kg weight hammer was fixed on a certain height, and the hammer was allowed to drop freely on the impact test sheet, and whether there were cracks and peeling phenomenon of the paint film was observed. The maximum height of the paint film without rupture was the impact strength. The AG-IC100KN precision universal mechanical testing machine (Dongguan Seput Testing Equipment Co., Ltd., Dongguan, China) was used to measure the elongation at break of the paint film. The paint film was coated on the glass substrate and peeled off with a knife after being dried. The two ends of the paint film were fixed with a clamp, and the paint film was stretched at a speed of 0.12 mm/min and broken under a certain longitudinal load. L₀ represented the initial value of the distance between the clampers, Lₐ represented the distance of the clampers when it is broken. The elongation at break (e) of the paint film can be calculated by Equation (2)

\[ e = \frac{(Lₐ - L₀)}{L₀} \times 100\% \]  

(2)

The liquid resistance of the paint film was tested by 15.0% NaCl, red ink, 70.0% medical ethanol, white cat detergent which contained 25.0% fatty alcohol ethylene oxide and 75.0% water. The filter paper was soaked in the test solution, taken out with tweezers and placed on the sample. Five layers of paper were placed on each test area and covered with glass. After 24 h, the circular paper was peeled off, then the residual liquid was sucked up with filter paper, and the color difference and the gloss of the paint film surface were observed [29]. When American lime is heated above 160 °C, the discoloration is serious, and it is easy to deform and crack at high temperature due to the wet expansion and dry shrinkage. Therefore, the maximum temperature of 160 °C is selected as the limit value. Aging and stability tests were carried out in the oven at temperatures of 120 and 160 °C, and a ZN ultraviolet weather resistance test chamber (Shenzhen Changxu Machinery Equipment Co., Ltd., Shenzhen, China). Then, the color difference and gloss of the paint film were tested. The aging time of oven was set as 40 h, and that of the UV weathering test chamber was 200 h. The damage of the paint films with microcapsules and without microcapsules in different aging environments was compared.

The standard deviation analysis method is used for statistical analysis of data. In short, standard deviation is a measurement concept of the degree to which a set of values are dispersed from the average value. A large standard deviation means that there is a big difference between most values and their average values; a small standard deviation means that these values are closer to the average. N is the number of the total number, \( \chi_i \) is the i-th data and \( \mu \) is the average value. The standard deviation (\( \sigma \)) was calculated by Equation (3)

\[ \sigma = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (\chi_i - \mu)^2} \]  

(3)

All the tests were repeated four times, and the error was within 5.0%.
3. Results and Discussion

3.1. SEM and FTIR of the Microcapsules

The SEM micrographs of microcapsules were shown in Figure 2. As shown in Figure 2, the spherical microcapsules with relatively uniform particle size of about 5 μm were prepared. It can be seen from Figure 3 that the peaks at 3354, 2973, 1633 and 1554 cm\(^{-1}\) were caused by the tensile vibration of N–H, C–H, C=O and C–N, and the appearance of characteristic peaks of these functional groups proved the existence of UF resin in the microcapsules. The peak value of 1742 cm\(^{-1}\) was caused by C=O tensile vibration in waterborne acrylic resin, indicating the existence of waterborne emulsion in the microcapsule, and its chemical structure was not damaged.

![Figure 2. SEM of UF with waterborne emulsion microcapsules: (A) low and (B) high magnification.](image1)

![Figure 3. FTIR of urea-formaldehyde (UF) with waterborne emulsion microcapsules.](image2)

3.2. Effect of Coating Process on Optical Properties

The influence of coating process on the color difference of the paint film with microcapsules was shown in Table 3. The data in Table 3 are expressed as \( \mu \pm \sigma \). It can be seen that the standard deviation is in a small range, indicating that the experimental data are relatively stable and have reference value. The results showed that the color differences of the waterborne paint film prepared by different coating process were less than 1.1, and the color difference did not change with the change in coating...
process, indicating that the coating process had no effect on the color difference of waterborne paint film with microcapsules.

Table 3. Effect of the coating process on the color difference of the paint film with microcapsules.

| Sample          | L1 | a1 | b1 | c1 | H1 | L2 | a2 | b2 | c2 | H2 | ∆E |
|-----------------|----|----|----|----|----|----|----|----|----|----|----|
| No microcapsules| 71.8 ± 1.7 | 13.7 ± 0.3 | 31.6 ± 0.7 | 34.4 ± 0.8 | 66.5 ± 1.6 | 72.1 ± 1.8 | 13.4 ± 0.3 | 31.5 ± 0.7 | 34.1 ± 0.8 | 66.3 ± 1.6 | 0.4 ± 0 |
| 1#              | 71.8 ± 1.7 | 12.0 ± 0.3 | 28.0 ± 0.7 | 30.5 ± 0.7 | 66.6 ± 1.6 | 72.3 ± 1.8 | 11.9 ± 0.2 | 28.0 ± 0.7 | 30.4 ± 0.7 | 66.8 ± 1.6 | 0.5 ± 0 |
| 2#              | 75.5 ± 1.8 | 10.7 ± 0.2 | 25.6 ± 0.6 | 27.8 ± 0.6 | 67.2 ± 1.6 | 76.0 ± 1.9 | 10.1 ± 0.2 | 25.9 ± 0.6 | 28.6 ± 0.7 | 69.2 ± 1.7 | 0.8 ± 0 |
| 3#              | 69.2 ± 1.7 | 13.9 ± 0.3 | 31.5 ± 0.7 | 34.4 ± 0.8 | 66.1 ± 1.6 | 69.4 ± 1.7 | 14.2 ± 0.3 | 30.7 ± 0.7 | 33.8 ± 0.8 | 65.1 ± 1.6 | 0.9 ± 0 |
| 4#              | 77.1 ± 1.9 | 10.4 ± 0.2 | 32.0 ± 0.8 | 33.7 ± 0.8 | 71.9 ± 1.7 | 77.8 ± 1.9 | 10.8 ± 0.2 | 32.7 ± 0.8 | 70.5 ± 1.8 | 0.9 ± 0 |
| 5#              | 70.2 ± 1.7 | 15.7 ± 0.3 | 32.3 ± 0.8 | 35.9 ± 0.9 | 64.0 ± 1.6 | 70.7 ± 1.7 | 14.8 ± 0.3 | 31.8 ± 0.7 | 35.1 ± 0.9 | 64.9 ± 1.6 | 1.1 ± 0 |
| 6#              | 72.2 ± 1.8 | 11.9 ± 0.2 | 32.5 ± 0.8 | 34.7 ± 0.8 | 69.9 ± 1.7 | 71.3 ± 1.7 | 12.2 ± 0.3 | 32.6 ± 0.8 | 34.8 ± 0.8 | 69.5 ± 1.7 | 1.0 ± 0 |
| 7#              | 73.7 ± 1.8 | 12.4 ± 0.3 | 31.5 ± 0.7 | 33.9 ± 0.8 | 68.2 ± 1.7 | 72.9 ± 1.8 | 13.0 ± 0.3 | 31.6 ± 0.7 | 34.2 ± 0.8 | 67.5 ± 1.6 | 0.9 ± 0 |
| 8#              | 69.6 ± 1.7 | 14.2 ± 0.3 | 31.6 ± 0.7 | 34.7 ± 0.8 | 65.7 ± 1.6 | 69.1 ± 1.7 | 14.5 ± 0.4 | 31.8 ± 0.7 | 35.0 ± 0.9 | 65.4 ± 1.6 | 0.6 ± 0 |

The gloss of the paint film under different coating process was measured at three incident angles of 20°, 60° and 85°. It can be seen from Table 4 that the gloss of No. 1–4# was higher than that of No. 5–8#, that is, the gloss of paint film with microcapsules in primer was better than that of topcoat. The reason was that when microcapsules were added to the topcoat, the particles on the topcoat would be enhanced, the surface roughness would be increased, and the diffuse reflection phenomenon would be enhanced, thus the gloss of the paint film would be decreased [30]. Compared with No. 1–4# samples, when the microcapsules were added in primer, No. 3# with “3 layers of primer, 2 layers of topcoat and microcapsules added in primer” had the highest gloss, followed by No. 4# paint film with “3 layers of primer, 3 layers of topcoat and microcapsules added in primer”. This is because when the microcapsules were added in primer, the primer of No. 3# and 4# had more coated numbers than that of No. 1# and 2#, so the surface was smoother. Therefore, the gloss would be increased when the topcoat was continuously applied on the smooth surface. The results of gloss showed that the coating process of “3 layers of primer, 2 layers of topcoat, microcapsules added in primer” had little effect on the gloss of the paint film.

Table 4. Effect of the coating process on the gloss of the paint film with microcapsules.

| Sample          | 20° Gloss (%) | 60° Gloss (%) | 85° Gloss (%) |
|-----------------|---------------|---------------|---------------|
| No microcapsules| 7.3 ± 0.1     | 27.9 ± 0.6    | 30.7 ± 0.7    |
| 1#              | 5.6 ± 0.1     | 22.9 ± 0.5    | 39.0 ± 0.9    |
| 2#              | 4.1 ± 0.1     | 17.1 ± 0.4    | 49.7 ± 1.2    |
| 3#              | 8.3 ± 0.2     | 29.1 ± 0.7    | 53.3 ± 1.3    |
| 4#              | 7.1 ± 0.1     | 24.5 ± 0.6    | 40.7 ± 1.0    |
| 5#              | 1.9 ± 0       | 7.3 ± 0.1     | 22.1 ± 0.5    |
| 6#              | 2.5 ± 0       | 10.0 ± 0.2    | 16.1 ± 0.4    |
| 7#              | 2.8 ± 0       | 10.8 ± 0.2    | 19.3 ± 0.4    |
| 8#              | 1.8 ± 0       | 7.2 ± 0.1     | 21.6 ± 0.5    |

3.3. Effect of Coating Process on Mechanical Properties

The results of hardness, adhesion, impact resistance and elongation at break of the paint film prepared by different coating process were shown in Table 5. The hardness grades of No. 1–8# were 2H-3H. There was no significant difference between adding microcapsules in primer and adding in topcoat. The number of primer and topcoat had a slight effect on the hardness, which was mainly due to the uneven distribution of microcapsule particles in the coating process [31]. The adhesion of No. 1–8# paint film was good, which was basically grade 0, except that No. 6# and No. 8# were grade 1. For No. 6 and No. 8, the surface adhesion is slightly reduced, which is due to the excessive coating times after adding microcapsules into the topcoat. The impact resistance of No. 1–8# was basically 100.0 N-cm⁻², while that of No. 3# and No. 8# was slightly higher. From the experimental results of the elongation at break, after the microcapsules were added to the waterborne coatings, the elongation at break was significantly increased. This is because microcapsules are shell-shaped spheres. Under the
action of tensile force, the rupture of microcapsules will release healing agents, reduce the occurrence of cracks and significantly improve the toughness of the paint film [32]. There was little difference in elongation at break of the paint film, among which No. 3# and No. 5# had higher elongation at break. The mechanical properties of the paint film prepared by the coating process of “3 layers of primer, 2 layers of topcoat, microcapsules added in primer” was better. At this time, the paint film hardness grade was 3H, the adhesion grade was 0, the impact resistance was 110.0 N·cm⁻², and the elongation at break was 29.7%.

Table 5. Effect of the coating process on the mechanical properties of the paint film with microcapsules.

| Sample | Hardness | Adhesion (Grade) | Impact Resistance (N·cm⁻²) | Elongation at Break (%) |
|--------|----------|------------------|-----------------------------|------------------------|
| No microcapsules | HB ± 0 | 0 ± 0 | 50.0 ± 0 | 5.2 ± 0.1 |
| 1#      | 2H ± 0   | 0 ± 0 | 100.0 ± 0 | 20.1 ± 0.4 |
| 2#      | 3H ± 0   | 0 ± 0 | 100.0 ± 0 | 29.4 ± 0.7 |
| 3#      | 3H ± 0   | 0 ± 0 | 110.0 ± 0 | 29.7 ± 0.7 |
| 4#      | 2H ± 0   | 0 ± 0 | 100.0 ± 0 | 23.7 ± 0.5 |
| 5#      | 2H ± 0   | 0 ± 0 | 100.0 ± 0 | 29.8 ± 0.7 |
| 6#      | 3H ± 0   | 1 ± 0 | 100.0 ± 0 | 24.7 ± 0.6 |
| 7#      | 2H ± 0   | 0 ± 0 | 100.0 ± 0 | 26.6 ± 0.6 |
| 8#      | 3H ± 0   | 1 ± 0 | 110.0 ± 0 | 25.6 ± 0.6 |

The liquid resistance of the paint film prepared by different coating process was tested, shown in Table 6. The color of No. 1–8# had no change and the color difference was very small after the NaCl, ethanol and detergent liquid test. After the red ink test, the color difference increased. However, the color difference of the coatings with the microcapsules added to the primer was smaller than that of the topcoat. The reason for this is that after the microcapsules are added to the primer, the topcoat separates the white particles of the microcapsules from the red ink, so that the color difference does not change significantly. The gloss of No. 1–8# paint film was almost unchanged after the liquid resistance test of NaCl, ethanol, detergent and red ink. The liquid resistance of No. 1–8# paint film to NaCl, ethanol and detergent was grade 1, and there was no mark on the surface of the paint film. The liquid resistance level of red ink was different, ranging from 1 to 3. The liquid resistance of the paint film with microcapsules in the primer was better than that of the topcoat.
Table 6. Effect of coating process on liquid resistance of the paint film with microcapsules.

| Sample | Liquid Color Difference | Liquid Resistant Gloss (%) | Liquid Resistance (Grade) |
|--------|-------------------------|----------------------------|---------------------------|
|        | NaCl | Ethanol | Detergent | Red Ink | NaCl | Ethanol | Detergent | Red Ink | NaCl | Ethanol | Detergent | Red Ink | NaCl | Ethanol | Detergent | Red Ink |
| No microcapsules | 1.2 ± 0 | 0.3 ± 0 | 1.1 ± 0 | 1.7 ± 0 | 27.3 ± 0.5 | 27.9 ± 0.6 | 25.6 ± 0.5 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 |
| 1#     | 0.9 ± 0 | 1.0 ± 0 | 0.8 ± 0 | 2.5 ± 0 | 22.1 ± 0.5 | 22.7 ± 0.5 | 22.5 ± 0.5 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 |
| 2#     | 0.9 ± 0 | 0.7 ± 0 | 0.7 ± 0 | 2.7 ± 0 | 17.2 ± 0.4 | 17.1 ± 0.4 | 16.4 ± 0.4 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 |
| 3#     | 0.5 ± 0 | 1.2 ± 0 | 0.5 ± 0 | 1.9 ± 0 | 28.4 ± 0.7 | 28.7 ± 0.4 | 28.3 ± 0.7 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 |
| 4#     | 0.9 ± 0 | 0.9 ± 0 | 0.8 ± 0 | 2.2 ± 0 | 24.1 ± 0.6 | 24.3 ± 0.7 | 23.7 ± 0.6 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 |
| 5#     | 0.9 ± 0 | 0.9 ± 0 | 1.1 ± 0 | 5.5 ± 0.1 | 6.7 ± 0.1 | 6.9 ± 0.1 | 6.3 ± 0.1 | 5.6 ± 0.1 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 |
| 6#     | 1.1 ± 0 | 0.7 ± 0 | 0.8 ± 0 | 3.7 ± 0 | 9.4 ± 0.2 | 9.1 ± 0.2 | 9.7 ± 0.2 | 9.0 ± 0.2 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 |
| 7#     | 1.0 ± 0 | 0.7 ± 0 | 0.9 ± 0 | 4.0 ± 0.1 | 9.6 ± 0.2 | 10.1 ± 0.2 | 9.1 ± 0.2 | 8.7 ± 0.2 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 |
| 8#     | 1.3 ± 0 | 1.1 ± 0 | 1.2 ± 0 | 1.7 ± 0 | 7.4 ± 0.1 | 7.0 ± 0.1 | 7.2 ± 0.1 | 6.5 ± 0.1 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 | 1.0 ± 0 |
3.4. SEM and FTIR of the Paint Film

From the above results, it can be seen that the paint film with the coating process of “3 layers of primer, 2 layers of topcoat and microcapsules added in primer” had better performance. Under this coating process, the paint films with and without microcapsules were compared in Figure 4. It can be seen from Figure 4 that the paint film with microcapsules had few particles, uniform distribution and good morphology.

Figure 4. SEM of the paint film with “3 layers of primer, 2 layers of topcoat”: (A) 0; (B) 10.0% microcapsules in primer.

Figure 5 shows the infrared spectrum of the paint film. In the infrared spectrum of the paint film with microcapsules in the primer, the 3360 cm⁻¹ was N-H absorption peak, 2929 and 2865 cm⁻¹ were stretching vibration peaks of C-H, 1639 cm⁻¹ was attributed to C=O stretching vibration of UF resin, and the C=O characteristic peak was at 1730 cm⁻¹, which proved the existence of acrylic resin in microcapsules. In the infrared spectrum of the waterborne primer paint film without microcapsules, 2929, 2865 and 1447 cm⁻¹ were the stretching vibration peaks of –CH₂, and 1730 cm⁻¹ was the vibration absorption peak of C=O. There is no significant difference between the functional groups because the composition of the microcapsule core material was similar to that of the coatings.

Figure 5. FTIR of the paint film with “3 layers of primer, 2 layers of topcoat”: 0 and 10.0% microcapsule in primer.
3.5. Effect of Coating Process on Aging Resistance Properties

The paint films with microcapsules and without microcapsules prepared by the process of “3 layers of primer, 2 layers of topcoat” were put into a 120 °C oven, 160 °C oven and ultraviolet weather resistance test chamber for aging test. In the 120 °C oven (Figure 6), when the aging time of the paint film without microcapsules increased from 8 to 40 h, the color difference increased from 1.8 to 4.2, and the color difference of the paint film with microcapsules added in primer increased from 1.4 to 3.7. In the 160 °C oven (Figure 7), when the aging time of the paint film without microcapsules increased from 8 to 40 h, the color difference increased from 4.0 to 24.2, and the color difference in the paint film with microcapsules in primer increased from 2.0 to 22.1. When, in the UV weather resistance test chamber (Figure 8), the aging time of the paint film without microcapsules increased from 40 to 200 h, the color difference increased from 3.1 to 6.7, and the color difference in the paint film with microcapsules increased from 0.5 to 3.1. The results showed that the color difference in the paint film gradually increased with the increase in aging time. Moreover, in the same environment, after the same aging time, the color difference of the paint film without microcapsules increased more obviously than that of the paint film with microcapsules. This may be because the paint film with microcapsules will crack after aging, the core material emulsion (waterborne emulsion) repairs the microcracks and reduces the degree of discoloration [33].

The aging gloss of the paint film was observed at an incident angle of 60°. After the paint film was aged in 120 °C oven (Figure 9), the gloss of the paint film without microcapsules decreased from 61.2 to 55.8, while the gloss of the paint film with microcapsules in the primer slightly decreased from 30.9 to 29.2. After the paint film was aged in 160 °C oven (Figure 10), the gloss of the paint film without microcapsules decreased from 50.8 to 43.7, and that with microcapsules in primer decreased from 15.8 to 13.6. After the paint film was aged in the UV weather resistance test chamber (Figure 11), the gloss of the paint film without microcapsules decreased from 46.6 to 42.7, and the gloss of the paint film with microcapsules in primer decreased from 25.9 to 25.1. The results showed that the gloss of the paint film decreased with the increase in aging time and the gloss of the paint film without microcapsules decreased more obviously than that with microcapsules. This is because after aging for a certain period of time, the paint film would produce microcracks under the influence of the environment, so that the microcapsules rupture, and the healing agent outflows. Therefore, the healing agent can repair the microcracks and slow down the gloss [34].

![Figure 6. Effect of aging time on color difference of the paint film in the 120 °C oven.](image-url)
Figure 6. Effect of aging time on color difference of the paint film in the 120 °C oven.

Figure 7. Effect of aging time on color difference of the paint film in the 160 °C oven.

Figure 8. Effect of aging time on color difference in the paint film in the ultraviolet weather resistance test.

The aging gloss of the paint film was observed at an incident angle of 60°. After the paint film was aged in 120 °C oven (Figure 9), the gloss of the paint film without microcapsules decreased from 61.2 to 55.8, while the gloss of the paint film with microcapsules in the primer slightly decreased from 30.9 to 29.2. After the paint film was aged in 160 °C oven (Figure 10), the gloss of the paint film without microcapsules decreased from 50.8 to 43.7, and that with microcapsules in primer decreased from 15.8 to 13.6. After the paint film was aged in the UV weather resistance test chamber (Figure 11), the gloss of the paint film without microcapsules decreased from 46.6 to 42.7, and the gloss of the paint film with microcapsules in primer decreased from 25.9 to 25.1. The results showed that the gloss of the paint film decreased with the increase in aging time and the gloss of the paint film without microcapsules decreased more obviously than that with microcapsules. This is because after aging for a certain period of time, the paint film would produce microcracks under the influence of the environment, so that the microcapsules rupture, and the healing agent outflows. Therefore, the healing agent can repair the microcracks and slow down the gloss [34].

Figure 9. Effect of aging time on gloss of paint film in the 120 °C oven.

Figure 10. Effect of aging time on gloss of the paint film in the 160 °C oven.

Figure 11. Effect of aging time on gloss of paint film in the UV weather resistance test.
Figure 9. Effect of aging time on gloss of paint film in the 120 °C oven.

Figure 10. Effect of aging time on gloss of the paint film in the 160 °C oven.

Figure 11. Effect of aging time on gloss of the paint film in the ZN ultraviolet weather resistance test.

The SEM images of the paint films without microcapsules and with microcapsules before and after aging tested in the 120 °C oven, 160 °C oven and ultraviolet weather resistance are shown in Figures 12–14. The surface of the paint films without microcapsules is smooth in Figures 12A, 13A and 14A. Figures 12B, 13B and 14B show the paint film containing microcapsules in primer, with obvious particles on the surface. Figures 12C, 13C and 14C show the SEM pictures of the paint film without microcapsules after aging test. It can be seen that the paint film had obvious damage. The bubble cracks of a large size can be observed. The large crack diameter was close to 40–50 µm, accompanied by small diameter cracks. However, Figures 12D, 13D and 14D show that the paint film with microcapsules in primer had no obvious damage, and only a small number of bubbles with small diameter are observed. Microcapsules made the paint film have good elongation at break. Therefore, the paint film with the microcapsules added after aging test was not easily damaged due to its good toughness. Furthermore, under the action of environmental factors, the microcapsules would crack, and the healing agent could effectively repair the microcracks, while the paint film without microcapsules could not bear the impact of the environment and was prone to cracking [35]. The results showed that the paint film with microcapsules had better stability and aging resistance than those without microcapsules.
Figure 12. SEM of the paint film with and without microcapsules before and after aging in the 120 °C oven: before aging (A) without, (B) with microcapsules; after aging (C) without, (D) with microcapsules.

Figure 13. SEM of the paint film with and without microcapsules before and after aging in the 160 °C oven: before aging (A) without, (B) with microcapsules; after aging (C) without, (D) with microcapsules.
Figure 14. SEM of the paint film with and without microcapsules before and after aging in the ZN ultraviolet weather resistance test: before aging (A) without, (B) with microcapsules; after aging (C) without, (D) with microcapsules.

Figure 15 showed the infrared spectrum of the paint film without microcapsules before and after aging. The peaks at 2929, 2865 and 1447 cm$^{-1}$ were the stretching vibration peaks of –CH$_2$, and 1730 cm$^{-1}$ was the vibration absorption peak of C=O group. No peak disappeared or appeared before and after aging, indicating that there was no difference in the composition of the paint film without microcapsules before and after aging. Figure 16 showed the infrared spectrum of the paint film with microcapsules in primer before and after aging. The absorption peak of N–H was at 3360 cm$^{-1}$. The stretching vibration peak of C–H was at 2929 and 2865 cm$^{-1}$, and the tensile vibration peak of C=O group in the UF resin was at 1639 cm$^{-1}$. The C=O characteristic peak appeared at 1730 cm$^{-1}$ proved the existence of acrylic resin. No peak disappeared or appeared before and after aging, indicating that the composition of the paint film with microcapsules had no difference before and after aging. The results showed that after aging test, different aging environments had no effect on the composition of the paint film with and without microcapsules.
4. Conclusions

In this paper, the optical, mechanical properties and aging resistance of a waterborne paint film with microcapsules were studied to explore the best coating process. The microcapsules were prepared by using UF resin as wall material and waterborne emulsion as core materials, and the effects of different coating processes on the optical, mechanical and aging resistance properties of the paint film with microcapsules were studied on the surface of American lime. The paint film with microcapsules had better comprehensive performance with the coating process of “3 layers of primer, 2 layers of topcoat and microcapsules added in primer”. At this time, the paint film hardness grade was 3H, the adhesion was grade 0, the impact resistance was 110.0 N·cm$^{-2}$, and the elongation at break was 29.7%. The paint film with waterborne emulsion microcapsules had better stability. When waterborne...
acrylic coatings with UF with waterborne emulsion microcapsules were applied on American lime, the coating process of “3 layers of primer, 2 layers of topcoat and microcapsules added in primer” was recommended. The coatings obtained had good optical, mechanical and anti-aging properties, which provides a technical reference for the self-healing of waterborne coatings on wood surfaces.

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