coatings

Article

Tung Oil Microcapsules Prepared with Different Emulsifiers and Their Effects on the Properties of Coating Film

Pan Pan [1,2], Xiaoxing Yan [1,2,*] and Wenwen Peng [1,2]

1 Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Nanjing Forestry University, Nanjing 210037, China
2 College of Furnishings and Industrial Design, Nanjing Forestry University, Nanjing 210037, China
* Correspondence: yanxiaoxing@njfu.edu.cn

Abstract: In water-based coatings, the addition of tung oil microcapsules coated with urea formaldehyde resin (UF) can effectively repair the microcracks in the coating film on the surface of wood. The tung oil as a repairing agent plays an important role in the preparation of microcapsules. In this paper, Span-80, SDBS, OP-10, Tween-80 and SDS were used as five emulsifiers to study the influence of different emulsifiers on the preparation of tung oil microcapsules, and the properties of the coating film added to the waterborne coatings. According to the coating process of three bottoms and three sides, tung oil microcapsules were added to the water-based paint with a content of 12% and coated on the wood surface. The appearance and microstructure of the microcapsules, as well as the mechanical, optical and self-repairing properties of the paint film were analyzed to find out the best emulsifier suitable for the core material. The tung oil microcapsules prepared by Tween-80 have the best morphology, concentrated particle size distribution, particle size of 6–15 µm, and spherical morphology. The film with the microcapsules prepared by Tween-80 had the best performance, small color difference, high gloss, hardness of 5H, adhesion grade 1, elongation at break of 47.23%, impact resistance of 20 kg·cm, and good toughness. At the same time, the repair rate reached 37.9%. The results provide the application reference for the use of self-repairing microcapsules in coatings.

Keywords: emulsifier; film properties; microcapsules; self repair

Citation: Pan, P.; Yan, X.; Peng, W. Tung Oil Microcapsules Prepared with Different Emulsifiers and Their Effects on the Properties of Coating Film. *Coatings* **2022**, *12*, 1166. https:// doi.org/10.3390/ coatings12081166

Academic Editor: Marko Petric

Received: 13 July 2022
Accepted: 9 August 2022
Published: 12 August 2022

1. Introduction

To suppress the surface cracks of wooden furniture [1,2], the common method in the market is to brush a layer of protective paint on the surface of furniture [3–5], which can prevent the furniture surface from making contact with the air to protect the furniture. Among them, water-based coatings are widely used because of their fast drying speed, environmental protection, pollution resistance and other advantages [6,7]. The water-based paint on the surface of furniture can greatly increase the service life of furniture and beautify the furniture. However, the water-based coating film is affected by environmental factors and other factors in long-term use, which will lead to its own unstable performance and micro cracks [8]. If the coating film is not repaired in time, it will affect the overall structure of the film, which is also an urgent problem to be solved at present [9].

The microcapsules are a kind of encapsulation technology, which are widely used in biomedicine, coatings, building materials, etc. [10–13]. The core repair agent of self-repairing microcapsules is encapsulated by wall materials and directly buried in water-based coatings to protect the film. The vegetable oil microcapsules prepared by Song et al. [14] can protect the coating and realize repeated self-repair. The anti-corrosion self-healing coating developed by Han et al. [15] can significantly prolong the service life of the coating. The tung oil is a kind of green vegetable oil, which contains a lot of unsaturated fatty acids. The highly unsaturated conjugated system makes tung oil easy to oxidize into film [16,17]. Li et al. [18] confirmed the self-healing performance of microcapsules prepared from tung oil in scratch experiments. Ismail et al. [19] used tung oil to modify the self-healing performance of intelligent polymer coatings. The tung oil is an excellent choice for the core material of self-repairing microcapsules because of its fast drying, light specific gravity, good gloss, strong adhesion, heat resistance, acid resistance, corrosion resistance and good thermal stability [20]. Through the rupture of the capsule wall, the tung oil repair agent of the core material is promoted to flow to heal the crack in time and achieve the purpose of self-repair. Whether the core material can be successfully coated by the wall material is related to the emulsification process of the core material [21]. The core material is dispersed into tiny droplets by emulsification, and the size of droplets also determines the size of microcapsules. Therefore, the type and dosage of emulsifier play a vital role in the emulsification process of microcapsule core material [22], which affects the stability of microcapsule preparation process and the particle size of microcapsule.

As a surfactant, the emulsifier in microcapsules has both hydrophilic polar groups and lipophilic nonpolar groups [23,24]. Therefore, it can be adsorbed at the oil/water interface to form an interface facial mask with a certain strength. It has a protective effect on dispersed phase droplets, so that the dispersed phase droplets are not easy to coalesce when they collide with each other [25]. The key to the preparation of stable emulsion is to choose a suitable emulsifier, which is conducive to the preparation of microcapsules with uniform particle size and good surface morphology. Mao et al. [26] selected three different emulsifiers, OP-10, SDS and SDBS to prepare different microcapsules. The results showed that when SDBS was used as emulsifier, the microcapsules prepared were uniform in size and had good thermal stability. When the temperature reaches 265 °C, the core material will be released for effective repair and can be completely preserved in cement-based composites. Chung et al. [27] used Pluronic F-127, Tween-80 and SLS as different emulsifiers to prepare thyme oil microcapsules, and evaluated the influence of emulsifier and storage temperature on the release performance of microcapsules. The research showed that the type of emulsifier significantly affected the loading efficiency of thyme oil. The composite emulsifier prepared by Ma and others [28] can better control the particle size distribution and microstructure of microcapsules and achieve excellent anti-corrosion and antifouling functions. Tao et al. [29] coated shellac with melamine to prepare self-healing microcapsules. It was found that the hydrophilic lipophilic balance (HLB) value of emulsifier would affect the morphology, coating rate and performance of microcapsules. Yakdhane et al. [30] used the emulsifier Tween-80 to prepare flaxseed oil microcapsules in some cases, which will promote the development of functional foods and biopharmaceuticals. Therefore, in the preparation of microcapsules, the different emulsifiers need to be selected for different core materials to improve the output of microcapsules and enhance the performance of microcapsules.

To prepare microcapsules with good performance, the self-repairing tung oil microcapsules were prepared by in situ polymerization by changing the types of emulsifiers, comparing the types of different emulsifiers and HLB values. Therefore, five kinds of emulsifiers with different HLB values and types were selected with emulsifiers as changing factors. In this experiment, Span-80, SDBS, OP-10, Tween-80 and SDS were used as five different emulsifiers to study the emulsification process of core materials, the morphology and microstructure of microcapsules, and the performance of coating film to explore the effect of emulsifiers on microcapsules and the properties of film [31,32]. Through the analysis of the optical, the mechanical and the self-healing properties of the prepared microcapsules, the suitable emulsifiers were obtained. This study provides a basis for the further study of self-repairing microcapsules to improve the self-healing ability of tung oil microcapsules and broaden the application prospect.

2. Materials and Methods

2.1. Experimental Materials

The materials used in the preparation of microcapsules and paint films are shown in Table 1. The instruments used in the experiment are shown in Table 2. The viscosity of ethyl cellulose is 45.0–55.0 MPa·s, the loss on drying is ≤3.0 wt.% and the chloride is ≤0.1 wt.%. It is white or light brown powder under normal temperature. The waterborne primer is mainly composed of waterborne acrylic acid, copolymer dispersion dimmer additive and water, and the solid content is about 30.0%. The waterborne topcoat is mainly composed of waterborne acrylic acid, polyurethane synthetic additives and water, with a solid content of about 26.5%.

Table 1. List of experimental materials.

Reagent Name	Specification	Manufactor
ethyl cellulose	99.7%	Hebei Jinzhong cellulose Technology Co., Ltd., Nanning, China
37% formaldehyde solution	analytical purity	Nanjing Chemical Reagent Factory, Nanjing, China
urea	analytical purity	Nanjing Panfeng Chemical Co., Ltd., Nanjing, China
n-octanol	analytical purity	Jiangsu Anyi Chemical Co., Ltd., Nantong, China
citric acid monohydrate	analytical purity	Shandong lemon Biochemical Co., Ltd., Weifang, China
triethanolamine	analytical purity	Suqian Yongsheng fine chemical company, Suqian, China
sodium dodecyl benzene sulfonate (SDBS)	analytical purity	Tianjin Beichen Fangzheng reagent factory, Tianjin, China
sodium dodecyl sulfate (SDS)	analytical purity	Hebei kelondo Biotechnology Co., Ltd., Handan, China
Span-80	analytical purity	Shandong Zibo Haijie Chemical Co., Ltd., Zibo, China
Tween-80	analytical purity	Linyi younit Biotechnology Co., Ltd., Linyi, China
OP-10	analytical purity	Jinan Wilke Chemical Co., Ltd., Jinan, China
tung oil	analytical purity	Guangzhou Chaoya Chemical Co., Ltd., Guangzhou, China
dulux waterborne wood primer	-	Dulux Co., Ltd., Shanghai, China
dulux waterborne wood finish	-	Dulux Co., Ltd., Shanghai, China
board	-	Beijing Tiantan Furniture Co., Ltd., Beijing, China

Table 2. List of equipment in test.

Instrument	Specification	Manufactor
electronic balance	HZY-1202/2202	Huazhi Electronic Technology Co., Ltd., Fujian, China
magnetic stirrer	JZ-101S	Jiangsu Changchun Chemical Co., Ltd., Suzhou, China
circulating water multipurpose vacuum pump	SHB-III	Nanjing Panfeng Chemical Co., Ltd., Nanjing, China
tetrahedral film preparer	SZQ-4	Yunfan Instrument Co., Ltd., Tianjin, China
electric constant temperature blast drying oven	CK09-5E-DHG6310	Beijing haifuda Technology Co., Ltd., Beijing, China

2.2. Preparation Methods of Microcapsules with Different Emulsifiers

Cellulose modified urea formaldehyde resin wall material: 2.0 g of cellulose and 50 mL of water were mixed for use [33]. The 20.0 g urea and 27.0 g 37% formaldehyde water solution were proportioned in a 1:1 molar ratio and stirred with a magnetic stirrer. The temperature was controlled at 70 °C and the rotating speed was adjusted to 600 rpm/min. The triethanolamine was added dropwise during the reaction to adjust the pH value of the solution to 8. After 1 h of reaction, the cellulose solution was added to UF and dispersed by ultrasound for 30 min.

Preparation of tung oil for core material: the core wall ratio was fixed at 0.78:1, tung oil was weighed at 24.96 g, and the type of emulsifier was changed. The type of emulsifier and HLB value are shown in Table 3. Sample 1 was prepared with 2.496 g Span-80 and 247.104 g ethanol, and the content of the emulsifier was 1.0%. Sample 2 was mixed with 2.496 g SDBS as emulsifier and 247.104 g deionized water to obtain an emulsifier solution with a concentration of 1.0%. The preparation method of samples 3–5 was the same as that of sample 2. The main parameter of the experimental process is that the concentration of fixed emulsifier was 1.0%. The prepared emulsifier solution was added to the core material. The temperature of the magnetic stirrer was set to 45 °C, and the speed was adjusted to 1000 r/min. The tung oil can be fully emulsified for 30 min.

Table 3. Different emulsifier types and HLB values.

Sample (#)	Emulsifier	HLB Value	Emulsifier Type	Function
1	Span-80	4.3	nonionic type	It is oil soluble in liquid and insoluble in water, suitable for use as emulsifier of W/O emulsion.
2	SDBS	10.638	anionic type	It has the functions of dispersion and penetration. It can maintain the stability of the suspension.
3	OP-10	14.5	nonionic type	It is a commonly used non-ionic surfactant. When the water is added, it forms a large hydrophilic group to improve its hydrophilic ability.
4	Tween-80	15.0	nonionic type	It is a non-ionic surfactant with strong hydrophilicity. It is an excellent O/W emulsifier.
5	SDS	40.638	anionic type	It is an excellent anionic surfactant, soluble in water, and has good emulsifying, penetrating, decontaminating and dispersing properties.

Microencapsulation: The wall material mixed solution was slowly added to the core material solution. The citric acid monohydrate is mixed with deionized water to form a citric acid monohydrate solution with a concentration of 1.0% to adjust the solution of pH value to 3–4. The solution reaction temperature was 30 °C, the rotation speed was 900 r/min, and the reaction time was 2 h.

2.3. Preparation Method of Waterborne Coating Films

The coating process of three bottoms and three sides was adopted. The additional content of the water-based primer was 15.54 g, and the content of the tung oil microcapsule was 2.16 g, which was added to the water-based paint at the content of 12.0%. The primer was painted 3 times in total. The additional content of the water-based topcoat was the same as that of primer. It was added to the water-based paint and coated on the wood surface with a SZQ four-sided film preparer. Then it was put into the oven, and the temperature was set to 30 °C. After drying for 20 min, it was taken out and cooled to room temperature. It was polished with 800# sandpaper. The same operation was repeated three times. The primer had been completed. The finish paint was completed in the same way [34,35]. The preparation of water-based paint film was completed.

2.4. Testing and Characterization

Micro morphology test: Quanta-200 scanning electron microscope (SEM) (Fei, Oregon, OR, USA) and Zeiss sigma 300 optical microscope (OM) (Carl Zeiss, Oberkohen, Germany) are used to observe the micro morphology of microcapsules and paint films. The particle size of the SEM image of microcapsules was analyzed by Nano measurer software (V1.2).

Chemical composition test: The chemical composition of microcapsules is measured by vertex 80V infrared spectrometer (Brooke instruments, Shanghai, China). The transparent film is formed by pressing, and the absorption peaks are analyzed.

Paint film hardness test: QHQ pencil hardness tester (Shenzhen Forest Precision Instrument Co., Ltd., Guangzhou, China) is used to measure the hardness of paint film. According to GB/T 6739-2006 "Pencil Method for Determination of Film Hardness", the pencil of 6H-6B measures the hardness of the film. The included angle between the pencil and the film is 45°, and the pencil scratches a 3 mm long position on the surface of the film under the load of 1.0 kg. The scratch results are observed with a magnifying glass. The hardness of the pencil indicates the hardness of the coating.

Impact resistance test of paint film: QCJ-120 impact testing machine (Shenzhen sanuo Experimental Equipment Co., Ltd., Shenzhen, China) is used to measure the impact resistance of the paint film. According to GB/T 4893.9-2013 "Determination of Impact Resistance", the impact tip of the QCJ-120 impact testing machine is in the shape of a ball. The height of the ball hammer is fixed by screws, and the impact marks and cracks of the sample at the impact of the ball hammer are observed. The height of the ball hammer is recorded when the crack occurs. The impact strength of the film is expressed by the maximum height of 1.0 kg ball hammer impacting the film without causing damage.

Elongation at break test of paint film: The paint film is coated on the glass plate according to the coating process. After the paint film is dry, it is removed from the glass plate. Then MTest-I universal mechanical testing machine (Shanghai Yinti Precision Machinery Technology Co., Ltd., Shanghai, China) was used to test the elongation at break of the coating. The elongation at break of the paint film is calculated according to Formula (1). L_0 is the original length of the paint film, L is the length of the paint film when it breaks, and e is the elongation at break of the paint film [36].

$$\mathrm{e} = (L - L_0)/L_0 \times 100\% \tag{1}$$

Paint film adhesion test: QFH adhesion scriber tester (Hebei Zhongke Beigong Test Instrument Co., Ltd., Cangzhou, China) is used to test the adhesion of the coating. According to the national standard GB/T 4893.4-2013 "Determination of Adhesion by Cross Cutting", the hand-held cutter cuts at about 45° to the wood surface, with a spacing of 1 ± 0.01 mm, and the incision is as deep as the basswood. Then rotate the plate by 90° and cut it once to form a grid pattern. The grid is pasted with adhesive tape, and the adhesive tape is removed smoothly within 0.5–1.0 s at an angle of 60°. The adhesion of paint film is judged according to the grade standard.

Paint film roughness test: a Byes-3200 precision roughness tester (Shanghai Bangyi Precision Meter Co., Ltd., Shanghai, China) is used to test the roughness of paint film. The smoother the surface of the paint film, the smaller the R_a value.

Paint film color difference test: an HP-2136 Portable Colorimeter (Shanghai nocai Trading Co., Ltd., Shanghai, China) was used to test the color difference of the coating. The light source of color difference meter is D65. The lab color space is composed of brightness (L) and color channels (a) and (b). The L refers to lightness, and the larger the value, the brighter the surface chromaticity of the tested film; on the contrary, it is dark. The a indicates that the chromaticity changes from red to green, positive value indicates that the chromaticity is red; on the contrary, it is green. The b indicates that the chromaticity changes from yellow to blue, positive value indicates that the chromaticity is yellow; on the contrary, it is blue. The c is color saturation. Through the test of two places of the paint film, two sets of data are tested, which are ΔL, Δa and Δb, respectively. The calculation Formula (2) is as follows [37].]

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

Gloss test of paint film: LS195 gloss meter (Shenzhen Linshang Technology Co., Ltd., Shenzhen, China) is used to measure the gloss of paint film at 20°, 60° and 85°.

Self-repair performance test of paint film: A micro crack blade is respectively marked on the paint film. The size of the micro crack was observed by optical microscope. After the paint film is placed flat at room temperature for five days, the size of the same crack is observed with an optical microscope. The self-repair performance of the paint film is explored by observing the change in crack size twice.

All the above tests were carried out four times with an error of less than 5%.

3. Results and Discussion

3.1. Analysis of Micro Morphology of Microcapsules Prepared with Different Emulsifiers

Figure 1 shows the state of core material solution after emulsifying with different emulsifiers for half an hour. Figure 1A shows the core material emulsion with Span-80. After emulsification, there is obvious delamination, and the upper layer can be clearly seen as core material tung oil. It indicates that the core material is not fully reacted. It may be due to the low HLB value of emulsifier Span-80, which belongs to lipophilic emulsifier. It cannot disperse tung oil better, which leads to poor emulsifying effect. Figure 1B shows the core material solution with SDBS as emulsifier. The liquid is white, the emulsion is evenly dispersed, and there is less core material left in the upper part of the solution. Figure 1C shows the core material solution with emulsifier OP-10. The liquid in the lower layer is also evenly dispersed, and a small amount of foam is produced in the upper layer. Figure 1E also shows the SDS core emulsion of anionic emulsifier, with a large amount of white foam on the upper layer. This is mainly because anionic emulsifier is easy to produce foam in the process of high-speed rotating emulsifying core material, and the HLB value of emulsifier SDS is as high as 40.638, which may also be the reason for the generation of foam. Significantly, Figure 1D shows the core material emulsion with emulsifier Tween-80, without obvious delamination. The solution is evenly dispersed, the color is yellow, and there is no foam on the upper layer. It shows that tung oil is fully emulsified.

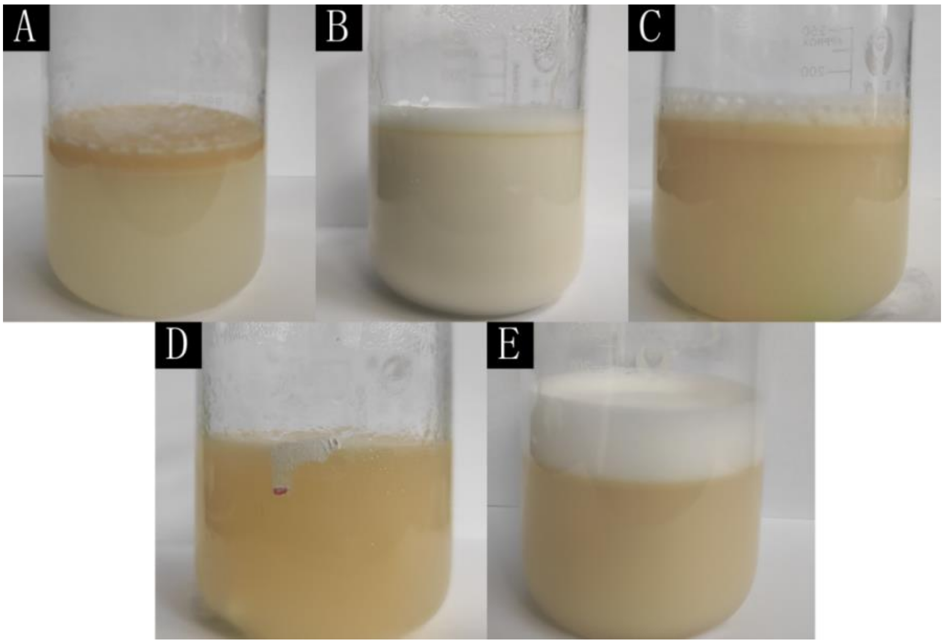

Figure 1. The core material emulsion emulsified by different emulsifiers: (**A**) Span-80, (**B**) SDBS, (**C**) OP-10, (**D**) Tween-80, (**E**) SDS.

Figure 2 is the SEM diagram of microcapsules under different emulsifiers. Figure 2A shows the microcapsule with emulsifier Span-80. The particle size is larger than that of microcapsules prepared by other emulsifiers, and the surface of microcapsules is not smooth. There is obvious adhesion between microcapsules, and the amounts of microcapsules produced is less. This may be because the tung oil core material is not completely emulsified in the emulsification process, which results in less microcapsules. Figure 2B,E show microcapsules with SDBS and SDS emulsifiers, respectively, which have small particle sizes and obvious agglomeration. There are few microcapsules prepared with SDS as emulsifier. This may also because the process of emulsifying core materials, large numbers of foam produced during the emulsification of SDS emulsifier, which affects the output of microcapsules. Figure 2C shows the microcapsules prepared with emulsifier OP-10, with small particle size but many cavities. This may be due to the gas generated when the core material is covered by the wall material, and it is not eliminated in time. When the microcapsules are finally dried, the bubbles will burst. This leads to the rupture of microcapsules [38]. In general, Figure 2D shows that the microcapsules prepared with Tween-80 as emulsifier have uniform particle size and the best morphology. There are also many microcapsules produced. It can also be proved that different core emulsifiers will affect the preparation of microcapsules.

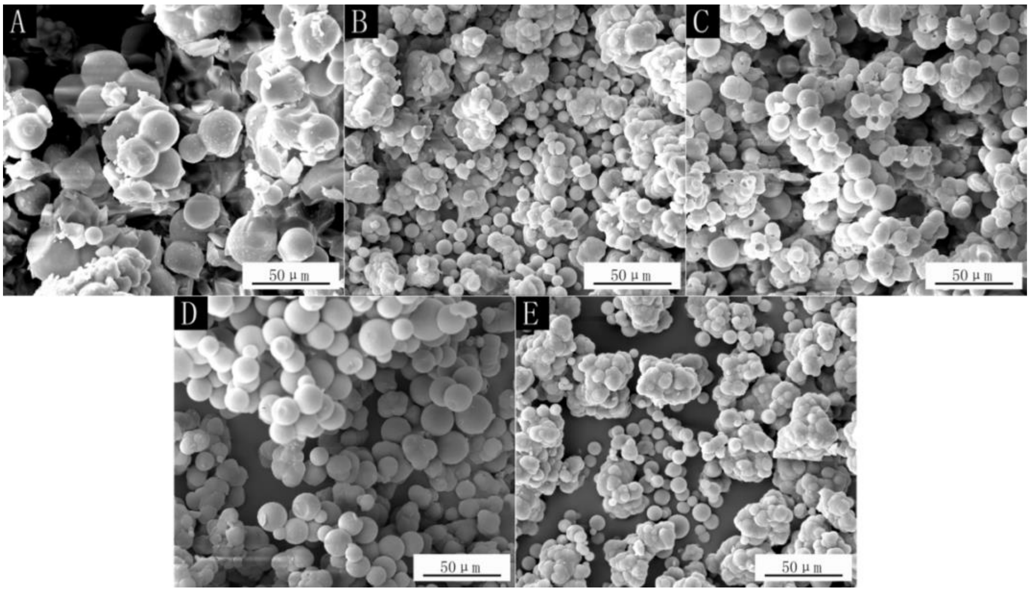

Figure 2. SEM of tung oil microcapsules emulsified by five emulsifiers (**A**) Span-80, (**B**) SDBS, (**C**) OP-10, (**D**) Tween-80, (**E**) SDS.

The emulsion can form microcapsules only when it is unstable. The emulsion changes from alkaline to acidic. At this time, the performance of lotion is reversed, and the solubility of core and wall materials is different, so the wall materials settle on the surface of the core materials to form the core wall ratio structure. The cellulose modified urea formaldehyde resin is used as the wall material and coated with the tung oil core material to form tung oil microcapsules.

3.2. Particle Size Analysis of Microcapsules Prepared with Different Emulsifiers

The particle size distribution of microcapsules prepared with different emulsifiers is shown in Figure 3. It can be seen from the figure that the particle size distribution of microcapsules with SDS as emulsifier is relatively dispersed, and the particle size is uneven. The particle size of microcapsules with emulsifiers OP-10 and Tween-80 is mainly between 6 and 15 μm. The percentages are 78% and 71%, respectively. The particle size of microcapsules with Span-80 emulsifier is mainly distributed in 11–20 μm. It accounts for about 67%. The size of microcapsules prepared with Span-80 as the emulsifier are slightly larger than that of other microcapsules. It can be proved that the type of emulsifier can affect the particle size of microcapsules.

3.3. Chemical Composition Analysis of Microcapsules Prepared with Different Emulsifiers

The infrared analysis results of microcapsules are shown in Figure 4. The 3384 cm^{-1} is the telescopic vibration peak superimposed by N–H and O–H. The absorption bimodal near 2965 cm^{-1} comes from the stretching vibration of methylene and various alkane configurations in the molecular structure of cellulose [33,39]. The characteristic absorption peak at 1380 cm^{-1} is caused by the stretching vibration of methyl groups [40]. These are the characteristic peaks of wall materials. The 2854 cm^{-1} is the stretching vibration peak of unsaturated bond C–H, and the 1746 cm^{-1} is the stretching vibration peak of C=O [33,41]. These are the characteristic peaks of tung oil. The core and wall materials of microcapsules can be found in the whole spectrum [42]. It can be proved that the microcapsule contains core and wall materials. It shows that the microcapsules prepared by the five emulsifiers are all successfully prepared.

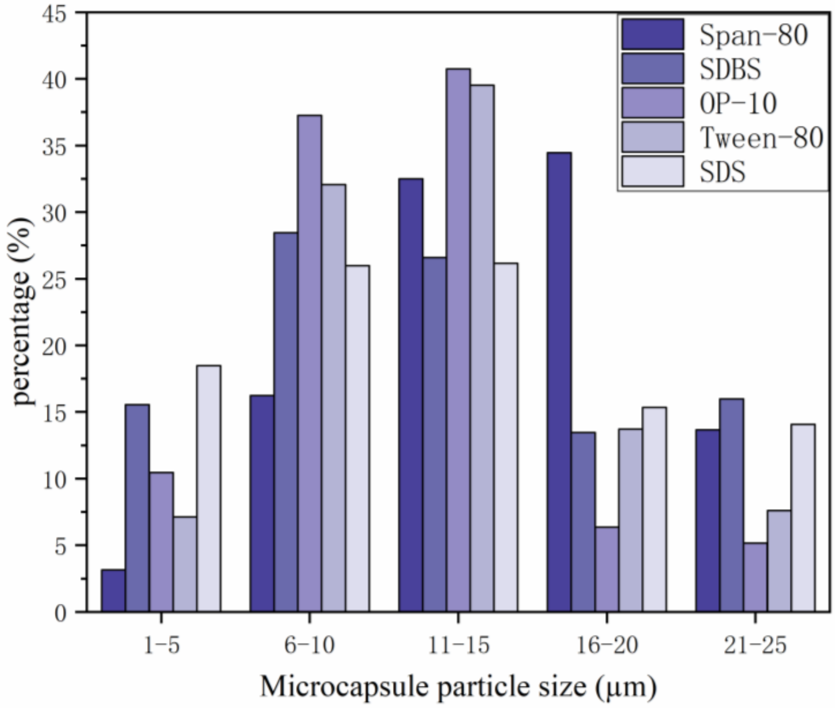

Figure 3. Particle size distribution of five emulsifier microcapsules.

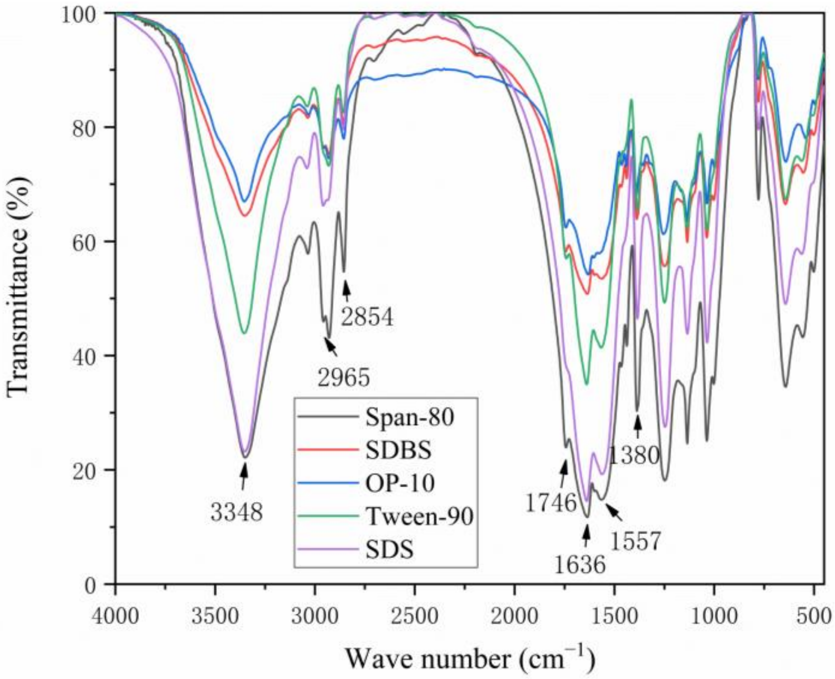

Figure 4. Infrared spectra of five emulsifier microcapsules.

3.4. Test of Film Properties of Microcapsules Prepared with Different Emulsifiers

3.4.1. Effect of Emulsifier on Color Difference and Gloss of Coating Film

The influence of microcapsules prepared with different emulsifiers on the color difference of paint film is shown in Table 4. It can be seen from the table that the color difference of the paint film of the microcapsules prepared by the five emulsifiers is similar. This is mainly because the microcapsules prepared by the five emulsifiers are white powder. There is not much difference in appearance, so the effect of coating on the wood surface is not much different [43]. However, the color difference value of the paint film without microcapsules is 3.5. The microcapsules prepared with Tween-80 as emulsifier are coated on the basswood, the color difference of the paint film is the smallest, with a color difference value of 4.1.

Table 4. Effect of emulsifier on chromatic aberration of coating film.

Emulsifier Type	Chromatic Aberration									
	L_1	a_1	b_1	L_2	a_2	b_2	ΔL	Δa	Δb	ΔE
Span-80	51.9 ± 1.7	29.1 ± 0.7	23.8 ± 0.5	49.9 ± 1.0	28.7 ± 0.8	25.3 ± 0.7	2.0 ± 0.1	0.4 ± 0.1	1.5 ± 0.2	6.4 ± 0.1
SDBS	46.0 ± 1.7	26.6 ± 0.6	21.3 ± 0.3	44.8 ± 1.8	28.2 ± 0.3	22.2 ± 0.4	1.2 ± 0.3	1.6 ± 0.1	0.9 ± 0.1	4.8 ± 0.1
OP-10	48.3 ± 1.6	20.2 ± 0.7	20.3 ± 0.4	47.7 ± 1.9	21.6 ± 0.7	22.1 ± 0.7	0.6 ± 0.3	1.4 ± 0.1	1.8 ± 0.3	5.5 ± 0.1
Tween-80	51.0 ± 0.9	26.6 ± 0.8	21.1 ± 0.6	52.6 ± 1.8	27.8 ± 0.5	21.4 ± 0.5	1.6 ± 0.1	1.2 ± 0.3	0.3	4.1 ± 0.1
SDS	56.7 ± 1.7	25.1 ± 0.7	27.1 ± 0.6	55.9 ± 1.6	27.3 ± 0.7	26.7 ± 0.6	0.8 ± 0.2	2.2 ± 0.2	0.4	5.6 ± 0.1

The influence of microcapsules with different emulsifiers on the gloss of paint film is shown in Table 5. The gloss of the paint film of microcapsules prepared with different emulsifiers is different. Among them, the gloss of the paint film with emulsifier Span-80, SDBS and SDS microcapsules is lower than that with emulsifier Tween-80 and without microcapsules. The gloss of the coating without microcapsules at 60° is 78.5, and that of Tween-80 microcapsule is 73.0. This is mainly because the microcapsule with Span-80 emulsifier has a larger particle size. This causes the paint film to become uneven when microcapsules are added to the film. The microcapsules with SDBS and SDS as emulsifiers have a large amount of agglomeration, which will also lead to uneven coating film [44,45]. Since microcapsules have been coated on the surface of basswood, the haze measurement cannot test the light transmittance of the paint film. Figure 5 shows the appearance of microcapsules prepared by different emulsifiers coated on the surface of basswood. Figure 5A shows that the surface of the paint film of the sample without microcapsules is transparent. By comparison, Tween-80 from Figure 5E has the best transparency of the coating film. The substrate texture is visible. The surface of other paint films has been covered with wood texture due to serious agglomeration of microcapsules, resulting in low transparency. To sum up, the gloss of the paint film of microcapsules with the emulsifier Tween-80 is better.

Table 5. Effect of emulsifier on gloss of coating film.

Emulsifier Type	60° Gloss (%)
No microcapsules	78.5 ± 1.13
Span-80	61.3 ± 1.77
SDBS	62.6 ± 1.65
OP-10	68.1 ± 2.01
Tween-80	73.0 ± 2.32
SDS	65.6 ± 1.68

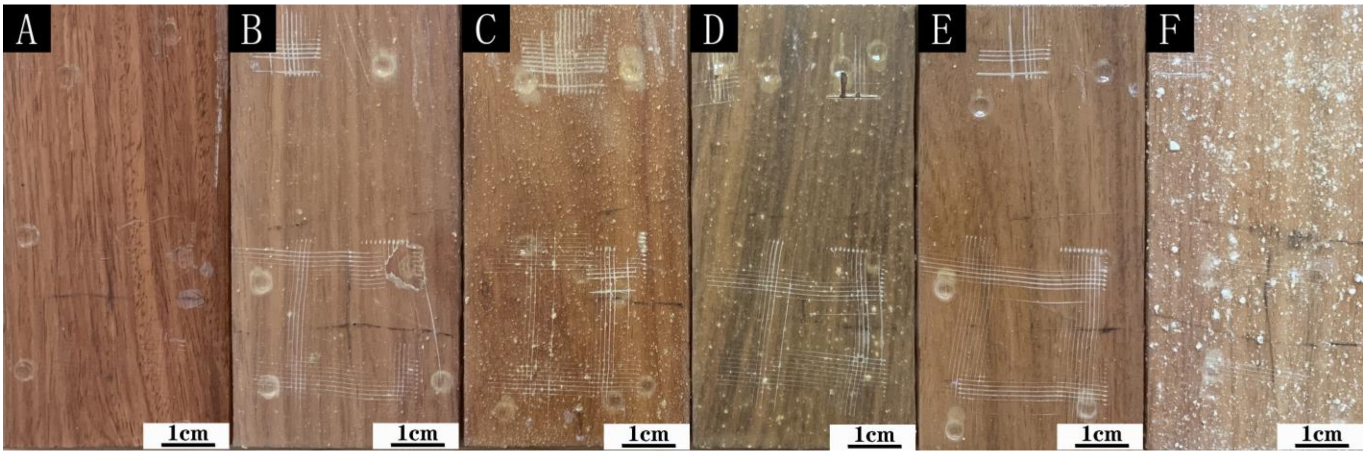

Figure 5. Morphology of paint film on the surface of basswood prepared with different emulsifiers (**A**) without microcapsules, (**B**) Span-80, (**C**) SDBS, (**D**) OP-10, (**E**) Tween-80, (**F**) SDS.

3.4.2. Effect of Emulsifier on Film Hardness and Adhesion

The influence of microcapsules with different emulsifiers on the hardness and adhesion of paint film is shown in Table 6. There is little difference in hardness between different paint films, and the hardness is between 4H–5H. The hardness of the coating without microcapsules is 3H and the adhesion is 0 grade. The film thickness is 60 μm. The paint film with better hardness is added with emulsifiers SDBS, OP-10 and Tween-80 microcapsules, respectively. The adhesion grade of paint film of microcapsules with different emulsifiers varies greatly. The adhesion grade of the paint film of microcapsules with emulsifiers Span-80, OP-10 and Tween-80 is 1. There is no obvious paint film falling off at the cutting intersection, and the falling off area is less than 5% of the total test area. The adhesion of the paint film of microcapsules with SDBS and SDS as emulsifiers is 2 and 3, respectively. The paint film falls off at the cutting intersection, and the falling area is large. Through comprehensive analysis, the hardness and adhesion of the paint film of microcapsules with emulsifier Tween-80 are the best.

Table 6. Effect of emulsifier on film hardness and adhesion.

Emulsifier Type	Hardness (H)	Adhesion (Grade)
No microcapsules	3	0
Span-80	4	1
SDBS	5	2
OP-10	4	1
Tween-80	5	1
SDS	5	3
Span-80	4	1

3.4.3. Effect of Emulsifier on Elongation at Break of Coating Film

Figure 6 shows the effect of microcapsules with different emulsifiers on the elongation at break of coating film. The elongation at break of the coating without microcapsules is 26.26%. It can be seen that the elongation at break of microcapsules with emulsifiers Span-80 and Tween-80 is higher; 47.08% and 47.23%, respectively. It shows that the coating films prepared by these two microcapsules have good toughness. It shows that different emulsifiers in microcapsules affect the performance of microcapsules. The elongation at break of the paint film of microcapsules with SDS as emulsifier was only 32.60%. It may also be because the prepared microcapsules have agglomeration. When added to water-based paint, it will affect the toughness of the paint film, thereby reducing the elongation at break of the paint film. In contrast, the microcapsules with emulsifiers Span-80 and Tween-80 have better performance.

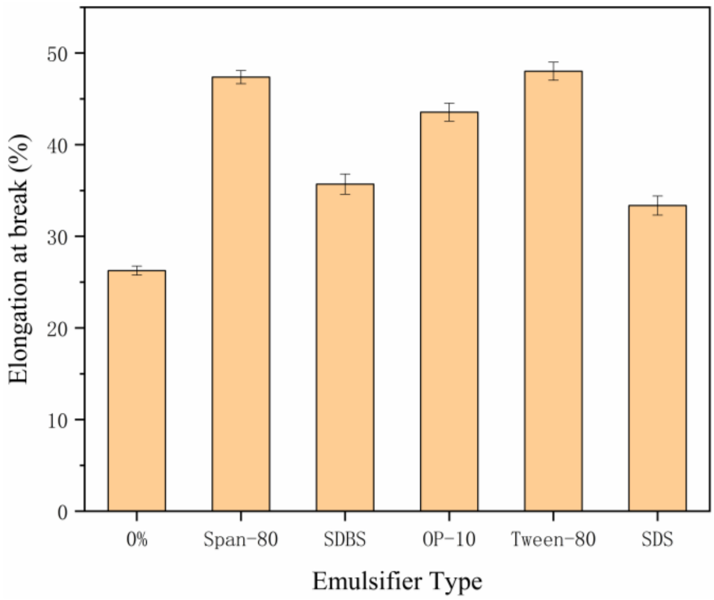

Figure 6. Effect of emulsifier on elongation at break of paint film.

3.4.4. Effect of Emulsifier on Impact Resistance of Paint Film

Figure 7 shows the impact resistance of paint films prepared by microcapsules of different emulsifiers. The impact resistance of the coating without microcapsules is 10 kg·cm. It can be seen from the figure that the impact resistance of the paint film with emulsifiers OP-10 and Tween-80 reaches 20 kg·cm. Secondly, the impact resistance of the paint film of microcapsules with Span-80 emulsifier is 19 kg·cm. Among the microcapsules prepared with five emulsifiers, the worst impact resistance of the paint film with SDS emulsifier is 12 kg·cm. This may be because the agglomeration of microcapsules affects the brittleness of the paint film. At the same time, it affects the force between the paint film and wood, so that the paint film and wood cannot be better bonded together. As a result, the impact resistance of the paint film is reduced [46]. The microcapsules with emulsifiers OP-10 and Tween-80 have better performance, so the paint film can be better connected with the wood surface to improve its impact resistance.

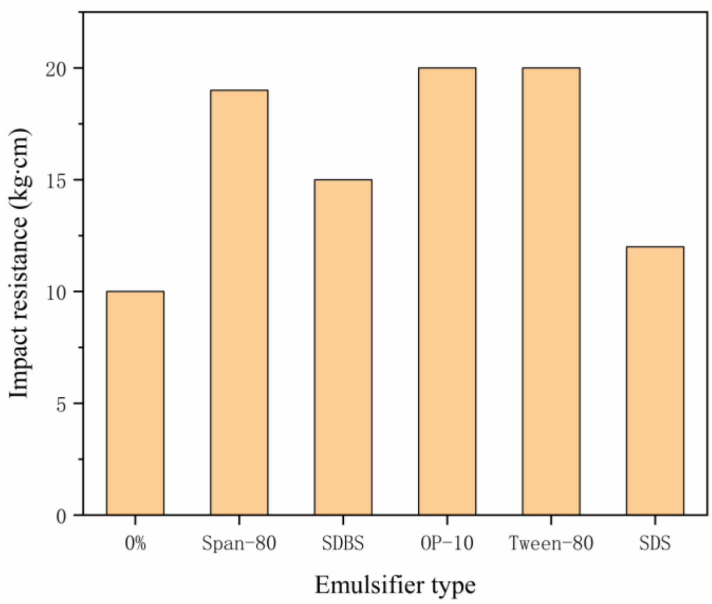

Figure 7. Effect of emulsifier on impact resistance of paint film.

3.4.5. Effect of Emulsifier on Film Roughness

Figure 8 shows the change in paint film roughness of microcapsules prepared with different emulsifiers. The roughness of the coating without microcapsules is 0.12 µm. It can be seen from the figure that the maximum roughness value of paint film with emulsifier SDS is 0.58 µm. The minimum roughness value of paint film with emulsifier Tween-80 is 0.29 µm. The roughness value of paint film prepared by other emulsifiers is 0.29–0.58 µm. The larger the roughness value is, the more uneven the paint film surface is. Therefore, the uneven surface of the paint film of microcapsules prepared by adding different emulsifiers may be caused by the agglomeration of microcapsules [47]. The surface of the paint film prepared with Span-80 and Tween-80 microcapsules as emulsifiers is relatively flat.

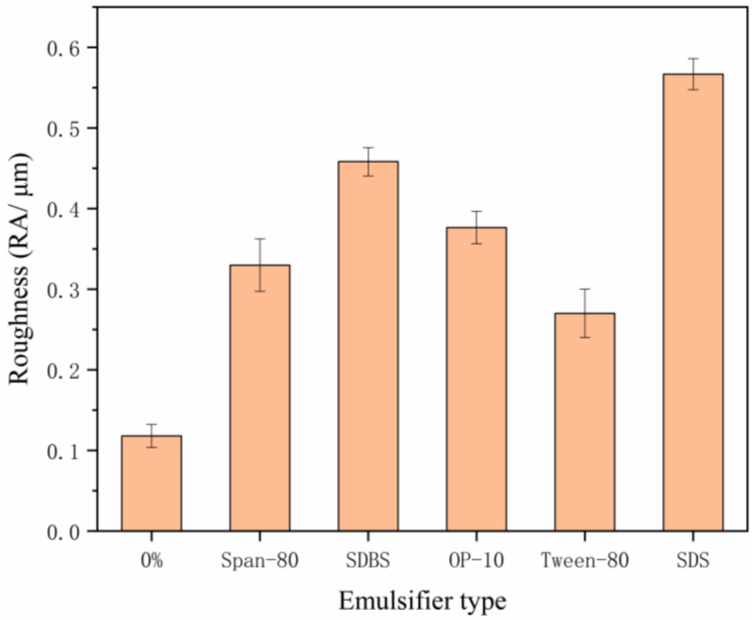

Figure 8. Effect of emulsifier on film roughness.

Through the above research on the color difference, gloss, hardness, adhesion, impact resistance, elongation at break and roughness of the paint film, it is concluded that the performance of the paint film of microcapsules is better with emulsifiers Tween-80 and OP-10. Then, the influence of microcapsules prepared by different emulsifiers on the coating film is explored by combining the surface roughness and foreign body sensation of the paint film. Figure 9 is the SEM diagram of the coating film. From the analysis of the SEM diagram, the appearance and performance of the film of microcapsules prepared with different emulsifiers are also different. The surface of the paint film with SDS and SDBS microcapsules as emulsifiers is very uneven, with obvious agglomeration and bubbling. The surface of the paint film with Span-80 microcapsule as emulsifier has obvious graininess, while the surface of the paint film with OP-10 and Tween-80 microcapsule as emulsifier is relatively flat and smooth, without obvious bubbling, and the coating effect is good. The film without microcapsules in Figure 9F is relatively smooth. Compared with it, emulsifier is the best membrane prepared by Tween-80.

3.5. Self-Repairing Properties of Microcapsules Prepared with Different Emulsifiers

Figure 10 shows the self-repairing properties of coating films prepared by microcapsules of different emulsifiers. By comparing the results of the first day and the fifth day and calculating the crack size, the self-healing properties of the paint film prepared by microcapsules with different emulsifiers were obtained. It can be seen from Figure 10A,B that the crack of the paint film with emulsifier Span-80 narrowed by 4.70 µm after five days. The repair rate was 22.15%. After repairing the paint film with SDBS as emulsifier, the crack was reduced by 2.64 µm, and the repair rate was 14.0% from Figure 10C,D. The cracks of the paint film with emulsifier OP-10 were reduced by 4.31 μm from Figure 10E,F, and the repair rate was 34.7%. The crack of paint film with emulsifier SDS was reduced by 1.25 μm from Figure 10I,J. The repair rate was 8.9%. However, the crack of paint film with emulsifier Tween-80 was reduced by 5.23 μm from Figure 10G,H. The repair rate was 37.9%. The repair performance of the paint film prepared by different emulsifier microcapsules is different, which shows that the type of emulsifier, particle size and coverage rate of microcapsules affect the repair performance of the coating film. However, it can be seen from Figure 10K,L that the crack of the paint film without tung oil microcapsule increased from 10.86 μm to 10.95 μm after 5 days; an increase of 0.09 μm. In general, the repair performance of the paint film with Tween-80 as emulsifier is better. The reason is that Tween-80 is a non-ionic surfactant with strong hydrophilicity and good emulsifying effect, which can effectively improve the self-repairing performance of tung oil microcapsules.

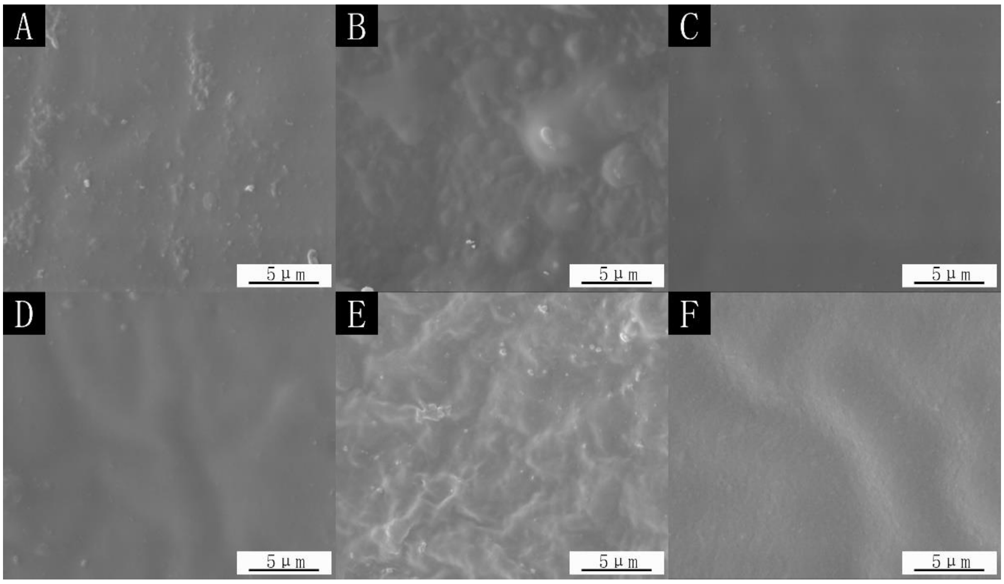

Figure 9. SEM of coating film: (**A**) Span-80, (**B**) SDBS, (**C**) OP-10, (**D**) Tween-80, (**E**) SDS, (**F**) no microcapsules.

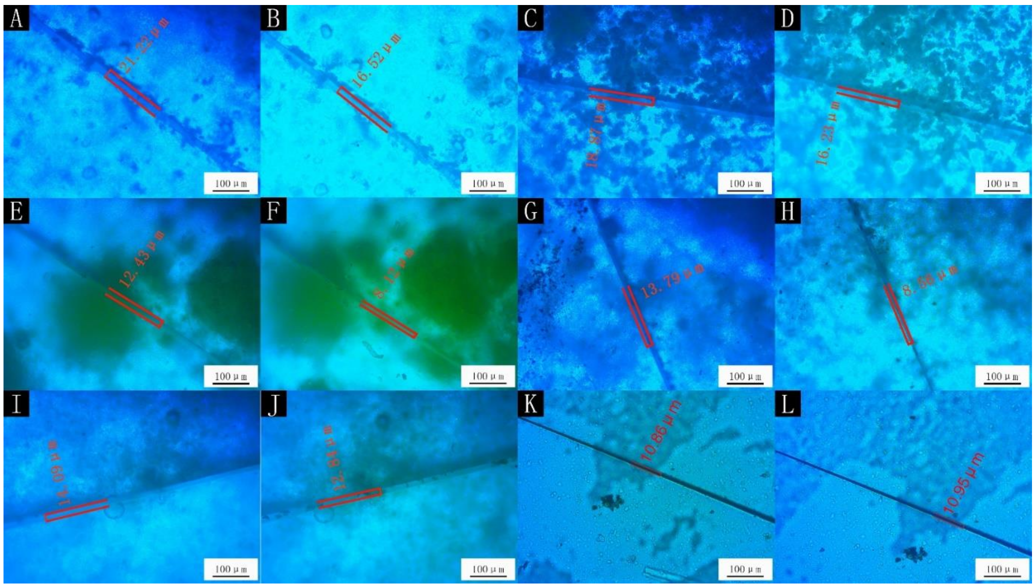

Figure 10. Micrographs of paint film self-healing test of five emulsifier microcapsules: (**A**) the first day of Span-80, (**B**) the fifth day of Span-80, (**C**) the first day of SDBS, (**D**) the fifth day of SDBS,

(**E**) the first day of OP-10, (**F**) the fifth day of OP-10, (**G**) the first day of Tween-80, (**H**) the fifth day of Tween-80, (**I**) the first day of SDS, (**J**) the fifth day of SDS, (**K**) the first day of no microcapsules, (**L**) the fifth day of no microcapsules.

The tung oil microcapsules can be stored directly in the air for two years or even longer. The microcapsules do not dissolve or precipitate in paint. The paint film with the prepared microcapsules has a stable performance within two years.

4. Conclusions

Different types of emulsifiers with HLB values affect the particle size and self-repairing performance of tung oil microcapsules. It can be concluded that the particle size of microcapsules prepared by Tween-80 as the emulsifier is 6–15 µm, and the appearance of the microcapsules is good. At the same time, tung oil microcapsules with a content of 12.0% are added to the primer and finish paint and coated on the wood surface. The obtained film has the best performance. The color difference of the paint film is 4.1, and the gloss of 60° is 73.0. The hardness of the paint film is 5H, the adhesion grade is grade 1, the elongation at break is 47.23%, and the impact resistance of the paint film is preferably 20.0 kg·cm, which has good toughness. The minimum roughness value is 0.29 µm. The microcapsule prepared by Tween-80 as emulsifier added to the waterborne paint has a good coating effect, and the crack repair rate is 37.9%. Therefore, based on the analysis of the microstructure of microcapsules and the performance of paint film, the Tween-80 emulsifier is suitable for the preparation of tung oil microcapsules to ensure the self-repairing effect of tung oil microcapsules. The results provide a reference for the application of self-repairing microcapsules in waterborne coatings.

Author Contributions: Conceptualization, methodology, validation, resources, data management, supervision, P.P.; Formal analysis, investigation, X.Y.; writing-review and editing, W.P. All authors have read and agreed to the published version of the manuscript.

Funding: This project was partly supported by the Postgraduate Research & Practice Innovation Program of Jiangsu Province (KYCX22_1098) and the Natural Science Foundation of Jiangsu Province (BK20201386).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Sjokvist, T.; Blom, A.; Walinder, M.E.P. The influence of heartwood, sapwood and density on moisture fluctuations and crack formations of coated Norway spruce in outdoor exposure. *J. Wood Sci.* **2019**, *65*, 45. [CrossRef]
2. Sjokvist, T.; Niklewski, J.; Blom, A. Effect of wood density and cracks on the moisture content of coated norway spruce (*Picea abies* (L.) Karst.). *Wood Fiber Sci.* **2019**, *51*, 160–172. [CrossRef]
3. Tomak, E.D.; Arican, F.; Gonultas, O.; Parmak, E.D.S. Influence of tannin containing coatings on weathering resistance of wood: Water based transparent and opaque coatings. *Polym. Degrad. Stabil.* **2018**, *151*, 152–159. [CrossRef]
4. Hu, J.; Liu, Y.; Wu, Z.; Pang, X. Construction of bionic structural color coating on wood surface based on polystyrene microspheres. *J. For. Eng.* **2021**, *6*, 35–42.
5. Zigon, J.; Kovac, J.; Petric, M. The influence of mechanical, physical and chemical pre-treatment processes of wood surface on the relationships of wood with a waterborne opaque coating. *Prog. Org. Coat.* **2022**, *162*, 106574. [CrossRef]
6. Lu, Z.; Hu, J.; Zhang, M.; Chang, S.; Liu, Y.; Zheng, L.; Li, X. Research on wettability of wood surface with waterborne-resin priming paint. *J. For. Eng.* **2021**, *6*, 178–183.
7. Yan, X.X.; Qian, X.Y.; Chang, Y.J. Preparation and Characterization of Urea Formaldehyde @ Epoxy Resin Microcapsule on Waterborne Wood Coatings. *Coatings* **2019**, *9*, 475. [CrossRef]
8. Lin, D.; Wang, X.; Zhang, M.; Yuan, S.C.; Xu, F.; Bao, D.; Wang, H.Y. A robust and eco-friendly waterborne anti-corrosion composite coating with multiple synergistic corrosion protections. *Compos. Part B-Eng.* **2022**, *232*, 109624. [CrossRef]
9. Feng, X.; Chen, J.; Wu, Z.; Wu, Y.; Gan, J. The formation mechanism of "skin-tactile" coating and its application and trends in. furniture. *J. For. Eng.* **2021**, *6*, 167–175.

10. Ge, L.Q.; Tan, X.; Sheng, R.W.; Xiao, J. Layer-by-layer self-assembly of giant polyelectrolyte microcapsules templated by mi-crobubbles as potential hydrophilic or hydrophobic drug delivery system. *J. Colloid Interface Sci.* **2022**, *47*, 100603. [CrossRef]
11. Yang, P.; Gao, X.; Wang, S.; Su, J.F.; Wang, L.Q. Novel waterproof bituminous coating using self-healing microcapsules containing ultraviolet light curing agent. *Constr. Build. Mater.* **2022**, *329*, 127189. [CrossRef]
12. Podgornik, B.B.; Sandric, S.; Kert, M. Microencapsulation for Functional Textile Coatings with Emphasis on Biodegradability-A Systematic Review. *Coatings* **2021**, *11*, 1371. [CrossRef]
13. Ouarga, A.; Lebaz, N.; Tarhini, M.; Noukrati, H.; Barroug, A.; Elaissari, A.; Ben Youcef, H. Towards smart self-healing coatings: Advances in micro/nano-encapsulation processes as carriers for anti-corrosion coatings development. *J. Mol. Liq.* **2022**, *354*, 118862. [CrossRef]
14. Song, Y.K.; Kim, H.W.; Chung, C.M. Repeatable Self-Healing of a Protective Coating Based on Vegetable-Oil-Loaded Microcapsules. *Polymers* **2022**, *14*, 2013. [CrossRef]
15. Han, R.; He, H.F.; Liu, X.; Zhao, L.F.; Yang, Y.; Liu, C.B.; Zeng, R.C. Anti-corrosion and self-healing coatings with polyaniline/epoxy copolymer-urea-formaldehyde microcapsules for rusty steel sheets. *J. Colloid Interf. Sci.* **2022**, *616*, 605–617. [CrossRef]
16. Shang, Q.; Jiang, W.; Lu, H.F.; Liang, B. Properties of Tung oil biodiesel and its blends with 0# diesel. *Bioresour. Technol.* **2010**, *101*, 826–828.
17. Fang, S.Q.; Zhang, H.; Zhang, B.J.; Li, G.Q. A study of Tung-oil-lime putty—A traditional lime based mortar. *Int. J. Adhes. Adhes.* **2014**, *48*, 224–230. [CrossRef]
18. Li, J.Y.; Shi, H.W.; Liu, F.C.; Han, E.H. Self-healing epoxy coating based on tung oil-containing microcapsules for corrosion protection. *Prog. Org. Coat.* **2021**, *156*, 106236. [CrossRef]
19. Ismail, N.A.; Khan, A.; Fayyad, E.; Kahraman, R.; Abdullah, A.M.; Shakoor, R.A. Self-Healing Performance of Smart Polymeric Coatings Modified with Tung Oil and Linalyl Acetate. *Polymers* **2021**, *13*, 1609. [CrossRef]
20. Mustapha, A.N.; Al Mheiri, M.; Al Shehhi, N.; Rajput, N.; Joshi, S.; Antunes, A.; Al Teneiji, M. The Microencapsulation of Tung Oil with a Natural Hydrocolloid Emulsifier for Extrinsic Self-Healing Applications. *Polymers* **2022**, *14*, 1907. [CrossRef]
21. Li, Y.; Wu, C.H.; Wu, T.T.; Wang, L.P.; Chen, S.G.; Ding, T.; Hu, Y.Q. Preparation and characterization of citrus essential oils loaded in chitosan microcapsules by using different emulsifiers. *Int. J. Food Eng.* **2018**, *217*, 108–114. [CrossRef]
22. Chatterjee, S.; Judeh, Z.M.A. Impact of the type of emulsifier on the physicochemical characteristics of the prepared fish oil-loaded microcapsules. *J. Microencapsul.* **2017**, *34*, 366–382. [CrossRef]
23. Dutschk, V.; Chen, J.; Petzold, G.; Vogel, R.; Clausse, D.; Ravera, F.; Liggieri, L. The role of emulsifier in stabilization of emul-sions containing colloidal alumina particles. *Colloid. Surf. A* **2012**, *413*, 239–247. [CrossRef]
24. Fan, C.J.; Zhou, X.D. Effect of emulsifier on poly(urea-formaldehyde) microencapsulation of tetrachloroethylene. *Polym. Bull.* **2011**, *67*, 15–27. [CrossRef]
25. Nielsen, N.S.; Horn, A.F.; Jacobsen, C. Effect of emulsifier type, pH and iron on oxidative stability of 5% fish oil-in-water emulsions. *Eur. J. Lipid Sci. Technol.* **2013**, *115*, 874–889. [CrossRef]
26. Mao, Q.J.; Feng, X.J.; Liang, P. Characteristics of self-healing microcapsules for cementitious composites. *J. Wuhan Univ. Technol.* **2018**, *33*, 1108–1112. [CrossRef]
27. Chung, S.K.; Seo, J.Y.; Lim, J.H. Microencapsulation of essential oil for insect repellent in food packaging system. *Ital. J. Food Sci.* **2013**, *78*, E709–E714. [CrossRef]
28. Ma, Y.X.; Jiang, D.; Yang, Y.P.; Ma, L.; Zhou, J.; Huang, G.S. The Effect of Complex Emulsifier on the Structure of Tung Oil and Phenolic Amides Containing Microcapsules and Its Anti-Fouling and Anti-Corrosion Performances. *Coatings* **2022**, *12*, 447. [CrossRef]
29. Tao, Y.; Yan, X.X. Influence of HLB Value of Emulsifier on the Properties of Microcapsules and Self-Healing Properties of Waterborne Coatings. *Polymers* **2022**, *14*, 1304. [CrossRef]
30. Yakdhane, A.; Labidi, S.; Vatai, G. Microencapsulation of Flaxseed Oil-State of Art. *Processes* **2021**, *9*, 295. [CrossRef]
31. Liu, Q.; Gao, D.; Xu, W. Effect of paint process on the performance of modified poplar wood antique. *Coatings* **2021**, *11*, 1174. [CrossRef]
32. Liu, Q.; Gao, D.; Xu, W. Influence of the bottom color modification and material color modification process on the performance of modified poplar. *Coatings* **2021**, *11*, 660. [CrossRef]
33. Peng, W.W.; Yan, X.X. Preparation of Tung Oil Microcapsule and Its Effect on Wood Surface Coating. *Polymers* **2022**, *14*, 1536. [CrossRef]
34. Xu, W.; Fang, X.; Han, J.; Wu, Z. Effect of coating thickness on sound absorption property of four wood species commonly used for piano soundboards. *Wood Fiber Sci.* **2020**, *52*, 28–43. [CrossRef]
35. Liu, Q.; Gao, D.; Xu, W. Effect of sanding processes on the surface properties of modified poplar coated by primer compared with mahogany. *Coatings* **2020**, *10*, 856. [CrossRef]
36. Li, R.R.; He, C.J.; Wang, X.D. Evaluation and modeling of processability of laser removal technique for bamboo outer layer. *JOM* **2021**, *73*, 2423–2430. [CrossRef]
37. Liu, Y.; Hu, J. Investigation of polystyrene-based microspheres from different copolymers and their structural color coatings on wood surface. *Coatings* **2021**, *11*, 14. [CrossRef]
38. White, A.L.; Langton, C.; Wille, M.L.; Hitchcock, J.; Cayre, O.J.; Biggs, S.; Blakey, I.; Whittaker, A.K.; Rose, S.; Puttick, S. Ultrasound-triggered release from metal shell microcapsules. *J. Colloid Interf. Sci.* **2019**, *554*, 444–452. [CrossRef]

39. Samadzadeh, M.; Boura, S.H.; Peikari, M.; Kasiriha, S.M.; Ashrafi, A. A review on self-healing coatings based on micro/nanocapsules. *Prog. Org. Coat.* **2010**, *68*, 159–164. [CrossRef]
40. Yan, X.X.; Pan, P. Preparation of Silver Antibacterial Agents with Different Forms and Their Effects on the Properties of Water-Based Primer on Tilia europaea Surface. *Coatings* **2021**, *11*, 1066. [CrossRef]
41. Yan, X.X.; Chang, Y.J. Investigation of waterborne thermochromic topcoat film with color-changing microcapsules on Chinese fir surface. *Prog. Org. Coat.* **2019**, *136*, 105262. [CrossRef]
42. Fu, R.; Zhang, W.; Li, D.; Zhang, H. Analyses on chemical composition of ancient wood structural component by using near infrared spectroscopy. *J. For. Eng.* **2021**, *6*, 114–119.
43. Liu, Y.; Hu, J.; Wu, Z. Fabrication of coatings with structural color on a wood surface. *Coatings* **2020**, *10*, 32. [CrossRef]
44. Zhao, Y.; Ren, J.; Zheng, X.; Pan, B.; Leng, W. Effects of three kinds of fungi on color, chemical composition and route of infection of *Picea sitchensis*. *J. For. Eng.* **2021**, *6*, 88–93.
45. Yan, X.X. Effect of Different Color Paste on Properties of Fluorine Resin/Aluminum Infrared Low Emissivity Coating. *Coatings* **2020**, *10*, 70. [CrossRef]
46. Seyedlar, R.M.; Imani, M.; Mirabedini, S.M. Bio-based furan coatings: Adhesion, mechanical and thermal properties. *Polym. Bull.* **2021**, *78*, 577–599. [CrossRef]
47. Elesini, U.S.; Leskovsek, M.; Bernik, S.; Sumiga, B.; Urbas, R. Influence of co-current spray drying conditions on agglomeration of melamine-formaldehyde microcapsules. *Dry. Technol.* **2016**, *34*, 1510–1520. [CrossRef]