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A study of Tung-oil–lime putty—A traditional lime based mortar

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ABSTRACT

Tung-oil-lime mortar is a special organic–inorganic binding material invented by the ancient Chinese people. It was widely used in wooden ship and special moisture-proof structures of ancient buildings due to its good sealing and waterproof performances. As a traditional binding material, tung-oil–lime mortar would have a bright applicative prospect in protection of cultural relics. In this paper, the formula, performances and mechanism of tung-oil–lime mortar are discussed. The results show that the mortar prepared by tung-oil with calcium hydroxide has better mechanical properties, water-resistivity and weather resistance than common lime mortar. The effective compositions of tung-oil–lime mortar were carboxylic acid calcium, curing tung-oil and calcium hydroxide. And these good performances of tung-oil–lime mortar come from the compact structure which is established through coordination reaction of Ca^{2+} from the $Ca(OH)_2$ and the oxidation aggregation reaction of C=C double bonds in unsaturated fatty acid.

1. Introduction

Nowadays, a large amount of ancient sites are suffering damage (some of them have even died out) with the development of society. How to maintain these treasures from generation to generation has become one of the hot topics at present. Unfortunately, many modern materials can't reach the demands of historic preservation although they have excellent performance. For example, the modern materials have poor compatibility with the ancient sites and usually would change the original exterior of cultural relics [1–5]. By contrast, the traditional materials raise conservators' interests and become the first choice of restoring the heritage due to their good performance and compatibility. Up to now, several traditional materials had been applied for repair of cultural relics successfully [5–8].

Tung-oil–lime mortar is a special organic–inorganic binding material which was widely used in ancient China. It is mainly composed of boiled tung oil and lime [9]. Sometimes in order to reinforce its cracking resistance and save raw materials, plant fibers can also be added. Due to its good water-resistivity, adhesive property, mothproofing [10] and stability, it was used in numerous fields. For instance, boaters used it to wad the fissures between boat decks, fill the cracks, scars, knags and worm holes on the deck surface, and prevent the nails – which played a crucial role in binding the hull – from corrosion [11]. As a sealing material, the invention of this material had profound influences on the shipbuilding technology and maritime exploration [10–13]. Stonemasons sometimes utilized it as adhesive to build rockeries and special structure of buildings to resist dampness [14]. In the "well salt" industry (mining salt mine), tung-oil–lime mortar plays a role as sealant to prevent leakage of pipelines [15]. Even in modern times the fishermen still adopt this material to repair small wooden fishing boats in some places of China.

As a kind of traditional adhesive material, tung-oil–lime mortar had withstood the tests of time. According to ancient records and archeological discoveries, the application of this mortar could date from about AD 581–AD 907. During the Ming Dynasty (AD 1368–AD 1664), there had been several literatures that recorded the detailed craftsmanship of tung-oil–lime mortar which indicate people had mastered this skill at that time [9,14]. However, for a long time the scientific knowledge of this material was scarce. Thus, its application in historic preservation is limited.

In this paper, the formula, early-life performances and scientific mechanism of tung-oil–lime mortar are discussed through the laboratorial model experiment and the analysis of ancient samples. We hope this work would help us understand the mechanism of this traditional material and provide a reliable formula for the application of this putty in practical historic restoration.

2. Materials and methods

2.1. Experimental materials and reagents

$Ca(OH)_2$ and $CaCO_3$ were purchased from the Sinopharm Chemical Reagent Incorporated Company. Tung-oil was purchased

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from a chemical plant in Jiangsu province, China. The ancient tung-oil–lime mortar samples are collected from the "Huaguang NO.1" ancient wooden ship (AD 1127–AD 1279) and a tomb in Zhejiang province, China (AD 1368–AD 1644), respectively. The tung-oil–lime mortar used on repairing modern wooden ships (10 years old) is offered by Museum of Overseas Communication History in Fujian province, China.

2.2. Experimental instrument

Typical LX-A hardness tester, Scanning electron microscopy (SEM), SIRION-100, FEI (America). X-ray diffraction (XRD), AXS D8 ADVANCE (Germany). Fourier transform infrared spectroscopy (FT-IR), NICOLET 560 (America).

2.3. Sample preparation

2.3.1. Preparation of ordinary lime mortar (control group)

Weigh a certain amount of $Ca(OH)_2$ and water ($m_{H_2O}/Ca(OH)_2=0.7$). Then stir clockwise (55–65 r/min) until the powders are converted into paste.

2.3.2. Preparation of tung-oil–lime mortar

Weigh lime and tung-oil according to different ratios. Then put them into a metal pail and grind until the mortar becomes fine and smooth. The original materials and ratio of modeling mortars in this research were shown in Table 1.

2.3.3. Preparation of samples

Since the tung-oil–lime mortar has high adhesiveness, using the traditional method to prepare samples will make the samples difficult to remove from the molds. Thus, in this paper the samples used in performance test were nonstandard. The specification of samples used in tests of compressive strength and corrosion resistance of chloride ion was $D=3.5$ cm, $H=4.0$ cm (D and H represent inner diameter and height of mold, respectively). And the specification of samples used in surface hardness test, water absorption and freeze–thaw resistance was $D=3.5$ cm, $H=2.0$ cm. The process of sample preparation is described as follows: first put the above mortar into molds (the inner face of molds had been daubed mold release agent) and vibrate until the molds are full of mortar. Then, the samples could be demoulded after 7 days. At last, transferring the samples into curing chamber (the condition of the curing chamber is $RH=(60\pm5)\%$, $T=(23\pm2)^{\circ}C$). In addition, the samples used in shear strength test were prepared by two sandstone (5 cm × 5 cm × 2.5 cm) bound with the above mortar.

3. Results and discussions

3.1. Mechanical property

The mechanical property of tung-oil–lime mortar was tested according to the standard test method of performance on building

Table 1
The composition and ratios of different lime mortar.

Serial number	Drying oil	Lime	Content of drying oil (% weight)
A	Tung-oil	$Ca(OH)_2$	17.5
B	Tung-oil	$Ca(OH)_2$	20
C	Tung-oil	$Ca(OH)_2$	22.5
D	Tung-oil	$Ca(OH)_2$	25
E	Tung-oil	$CaCO_3$	22.5
F (Control group)	–	$Ca(OH)_2$	-

Table 2
The results of mechanical properties of different mortars.

Serial number	Compressive strength (MPa)		Surface hardness (HD) (28 days)	Shear strength (N) (28 days)
	28 days	90 days		
A	0.18	0.48	46	48.74
B	0.20	0.50	49	56.36
C	0.20	0.60	56	56.04
D	0.18	0.62	57	54.89
E	< 0.05	< 0.05	< 10	–
F (Control group)	0.24	0.36	47	1.88

mortar (JGJ/T70-2009) [16]. The results were shown in Table 2. Comparing the mortar prepared by different lime and tung-oil, the compressive strength of the sample which was made by $CaCO_3$ and tung-oil was below 0.05 MPa after being maintained for 28 days and 90 days. This indicated that this tung-oil–lime mortar couldn't solidify even after 90 days in lab condition. Moreover, its surface hardness (< 10 HD) was also much lower than control group (47 HD). These data demonstrate that this mortar had hardly any pressure resistance. On the contrary, the sample made by $Ca(OH)_2$ and tung-oil had better mechanical strength. Its 28 days compressive strength (about 0.19 MPa) was close to the control group (0.24 MPa). And its 90 days compressive strength (about 0.55 MPa) and 28 days surface hardness (about 52 HD) were better than the control group (0.36 MPa and 47 HD, respectively). Furthermore, the 90 days compressive strength and 28 days surface hardness of $Ca(OH)_2$–tung oil mortar increased with the increasing of content of tung oil. While this growth trend slowed down when the content of tung oil reached 22.5–25% (sample C and D).

The adhesive property of these mortars also presented the similar rule as above. The mortar was made by $CaCO_3$ and tung oil without binding capacity. While the mortar made by $Ca(OH)_2$ and tung oil had good cohesiveness. Its adhesion was about 25 times larger than common lime mortar (control group). In conclusion, the mortar made by $Ca(OH)_2$ with tung-oil had better mechanical property. And the appropriate ratio of tung oil in mortar was about 22.5–25% from the aspect of mechanical property.

3.2. Weather resistance and waterproofness of different mortars

The weather resistance and water-resistivity of tung-oil–lime mortar were tested according to the standard test method of performance on building mortar (JGJ/T70-2009) [16] and natural stone test methods: Determination of water absorption coefficient by capillarity (EVS-EN 1925) [17], respectively. The mortar made by $CaCO_3$ and tung oil could hardly be used in cultural relics protection due to its weak mechanical property. Thus this kind of mortar was not tested in this part. The results were shown in Table 3. Common lime mortar broke down after 4 cycles of freezing and thawing. While the samples made by $Ca(OH)_2$ and tung oil failed after 6 to 7 cycles. This indicated mortar prepared by $Ca(OH)_2$ and tung oil had better weather resistance than the common lime mortar.

The water-resistivity test shows that the absorption coefficient of sample A to D reduced about 620 times than common lime mortar. And the results of Cl^- damage resistance test showed that the strength loss of sample A to D reduced about 10 times than common lime mortar. These results indicated mortar made by $Ca(OH)_2$ and tung oil had good waterproof and NaCl is not easy to seep into the mortar. These performances make this material work well as sealant on ships and dams.