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Quality Improvement of Lacquer from *Melanorrhoea usitata*

Introduction

Oriental lacquer has been used as a surface coating and embellishment on tableware and interior decoration for several thousand years in the Far East.[1] Lacquer can be applied to a number of materials such as wood, bamboo, paper, metal, porcelain, hide and cloth etc. In Thailand lacquerwork is classified as the applied arts. The design in gold leaves applied over black lacquer is used to decorate many objects for religious purposes and common use. The art of lacquering may protect and decorate small boxes, as well as entire wooden panels (cf. colour plate XVI.2). An extravagant example of lacquerwork (colour plate XVI.1) is preserved in the Royal State palanquin (*Rachentarayan*) for King Rama I (1782–1809 AD). It is made of wood, covered with lacquer and gold leaves, and decorated with glass. Inside the temple of Wat Pra Keaw Don Tao, in the province of Lampang, the ceiling and the walls are decorated with gilded lacquerwork and glass mosaic (colour plate XVI.3).

In the *Anacardiaceae* family, there are various kinds of lacquer trees used as a source for lacquer. *Rhus vernicifera* is the most important source of lacquer in China and Japan, whereas *Melanorrhoea usitata*, which is called *Huk Laung* in Thai, has been used as a source of lacquer in Burma and Thailand.[2] Investigations on the chemical composition of lacquer from *Huk Laung* showed, that the major constituents were (*Z,Z*)-3-heptadeca-8′,11′-dienyl) benzene-1,2-diol (1) (48 %) and its 4-isomer (2) (26 %). Eleven minor components (3–13), summarized in table 1[3–5], could be observed.

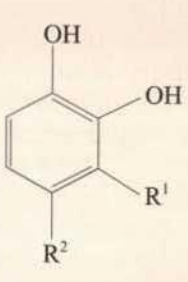
The nature of the hardening or setting reaction, usually referred to as 'drying', is known as a polymerization process with cross linking. In the past two decades, a few papers have been published concerning the polymerization of urushiol from *Rhus vernicifera*[6–7]. It has been suggested that the reaction involves an enzyme laccase and oxygen. It proceeds best in a humid atmosphere at a relatively low temperature. The polymerization mechanism of lacquer is quite complicated since it involves enzymic reactions. At present, there is no clear explanation for the behaviour of lacquer in the polymerization process.

After drying the lacquer coating does not only serve as a decorative finish, but also as a preservative and a protective coating. This surface coating has many advantageous properties, because it is water proof, rot proof and weather proof. However, the disadvantage of lacquer is, that it requires a long time for drying. Therefore the objective of the present study is to seek a method that could accelerate the drying process of lacquer.

Experiment

Lacquer of *Melanorrhoea usitata* was collected from the Chiang Mai province. The crude lacquer (1 kg) was dissolved in methanol. The mixture was stirred and standed for 48 hrs. It was filtered and the filtrate was evaporated under reducing pressure to produce a viscous black oil, which was used as a starting material in the next step. Adhesion measurements were carried out using the Tape Test (ASTM D3359–93). A sample

Table 1. Chemical Structures of Individual Components in Lacquer from *Melanorrhoea usitata*



	R¹	R²
(1)	(*Z,Z*)-heptadeca-8′,11′-dienyl	H
(2)	H	(*Z,Z*)-heptadeca-8′,11′-dienyl
(3)	(*Z*)-pentadec-7′-enyl	H
(4)	pentadecyl	H
(5)	H	pentadecyl
(6)	(*Z*)-heptadec-8′-enyl	H
(7)	(*E*)-heptadec-8′-enyl	H
(8)	H	(*Z*)-heptadec-8′-enyl
(9)	heptadecyl	H
(10)	10′-phenyldecyl	H
(11)	H	10′-phenyldecyl
(12)	12′-phenyldodecyl	H
(13)	H	12′-phenyldodecyl

was applied onto a wooden surface and dried for 7 days before testing.

A water resistancy test was carried out by applying the sample onto a thin stainless sheet (10 x 15 cm and about 1.2 mm thickness). After complete drying, it was immersed in water. The water temperature was kept at 40 ± 1 °C and the water was continuously stirred with air blowing. After 24 hrs the observation was continued.

Evaluation of the Optimum Temperature

Lacquer (10 g) was mixed with ammonium hydroxide (20 ml) and formaldehyde (30 ml) was slowly added in order to keep the temperature constant at 30 °C. The reaction mixture was continuously stirred at room temperature for 2 hrs. The organic layer was separated from the aqueous layer and washed with water until it was free from base. The product was dried under vacuum. Solubility tests showed, that the product did not dissolve in water and ethanol but dissolved in hexane, acetone and ethyl acetate. The surface drying time of the product was 24 hrs.

Lacquer (10 g) was mixed with ammonium hydroxide (20 ml) and formaldehyde (30 ml) and was refluxed on the oil bath at 130–140 °C for 1.5 hrs. The organic layer was separated and it soon solidified at room temperature. The product was washed with water until it was free from base and was dried under diminished pressure. Solubility tests showed, that the product did not dissolve in water and ethanol, but partly in hexane, acetone and ethyl acetate. The surface drying time of the product was 1 hr.

Evaluation of the Optimum Reagents

In this experiment the reaction was performed under the same conditions by reflux at 130–140 °C for 1.5 hrs. The mole of lacquer was kept constant while the mole of reagents, formaldehyde and ammonium hydroxide was varied from 0.25, 0.5, 1.0, 2.5, 5.0, 7.5, to 10.0 respectively. The product obtained from each experiment was subjected to the following tests: solubility, surface drying time, adhesion and water resistancy. The results of the tests are given below.

Lacquer: Reagents (1 : 0.25)
The product did not dissolve in water, but proved partly soluble in ethanol and soluble in hexane, acetone and ethyl acetate. Surface drying time of the product was 2 hrs. The adhesion on wood was classified as 4B and the product passed the water resistancy test.

Lacquer: Reagents (1 : 0.5)
The product did not dissolve in water and ethanol, proved partly soluble in hexane, but soluble in acetone and ethyl acetate. The surface drying time of the product was 1.5 hrs. The adhesion on wood was classified as 4B and the product passed the water resistancy test.

Lacquer: Reagents (1 : 1)
The product did not dissolve in water and ethanol, proved partly soluble in hexane and acetone and soluble in ethyl acetate. Surface drying time was 1 hr 20 min. The adhesion on wood was classified as 4B and the product passed the water resistancy test.

Lacquer: Reagents (1 : 2.5)
The product did not dissolve in water and ethanol, and proved partly soluble in hexane and acetone and soluble in ethyl acetate. The surface drying time of the product was 1 hr 10 min. The adhesion on wood was classified as 4B and the product passed the water resistancy test.

Lacquer: Reagents (1 : 5.0)
The product did not dissolve in water and ethanol, was partly soluble in hexane, acetone and soluble in ethyl acetate. The surface drying time was 50 min. The adhesion on wood was classified as 4B and the product passed the water resistancy test.

Lacquer: Reagents (1 : 7.5)
The product did not dissolve in water and ethanol, was partly soluble in hexane and acetone and soluble in ethyl acetate. The surface drying time was 40 min. The adhesion on wood was classified as 4B and the product passed the water resistancy test.

Lacquer: Reagents (1 : 10)
The product did not dissolve in water, ethanol and hexane, was partly soluble in acetone and soluble in ethyl acetate. The surface drying time was 35 min. The adhesion on wood was classified as 4B. The product passed the water resistancy test.

Lacquer
Lacquer did not dissolve in water, but proved soluble in ethanol, hexane, acetone and ethyl acetate. The surface drying time was more than 24 hrs. The adhesion on wood was classified as 4B. The lacquer passed the water resistancy test.

Results and Discussion

The main constituents in lacquer of *Huk Laung* are alkyl/alkenyl benzene-1,2-diols. The structure of the molecule is constructed with an aromatic nucleus and a long olefinic side chain. From the point of chemistry, polymerization can occur at both positions. An attempt was then made to accelerate the polymerization at the aromatic nucleus. Formaldehyde and ammonium hydroxide, a commercially available reagent, were used as a cross link agent. The lacquer was treated with formaldehyde and ammonium hydroxide to supply a product, which has the same physical properties as crude lacquer, but a 20 times faster surface drying time. When the reaction was carried out at ambient temperature, the surface drying time of the product was about 24 hrs. On the other hand, when increasing the temperature of the reaction up to 130–140 °C, the product needed a surface drying time of about 1 hr. Hence the optimum temperature of the reaction was 130–140 °C. Studies on the evaluation of the optimum reagents indicate, that when the amount of reagents was increased, the drying time of the product was decreased. However, a comparison of the physical properties of the products shows, that products prepared by using the mole ratio of lacquer and a reagent between 1 : 2.5–5.0 were suitable for the reaction. When the mole ratio was greater than 1 : 7.5, the product provided a faster drying time, but it lost its gloss after the water resistancy test.

Acknowledgements

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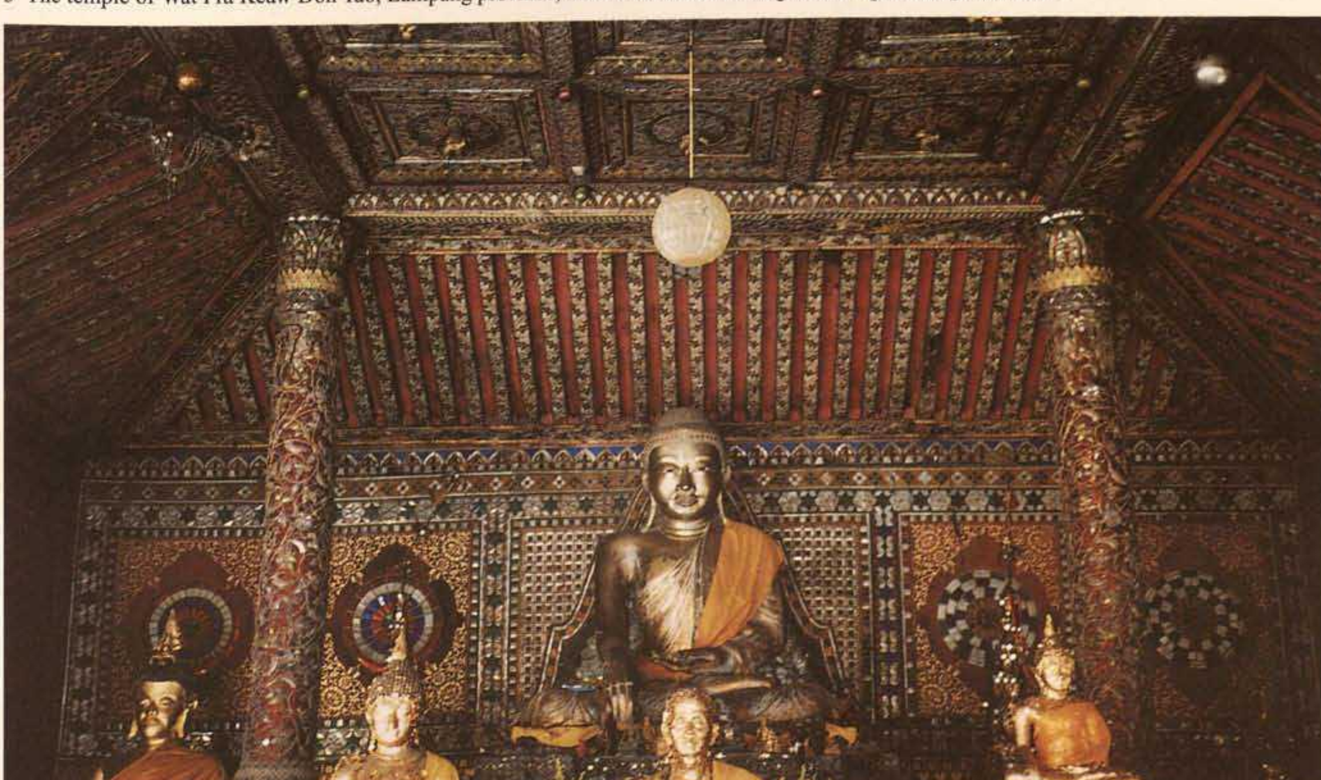
1 Royal State palanquin decorated with lacquer, gold leaves and colored glass

2 Bangkok, Wat Po, black lacquered door with gilded decoration

3 The temple of Wat Pra Keaw Don Tao, Lampang province, interior decorated with gilded lacquer and glass mosaic



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