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Optimal curing conditions for Korean *Dendropanax* lacquer

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Introduction

Korean *Dendropanax* lacquer is the resinous sap from *Dendropanax morbifera* Lev., which is found in the eastern area of Korea. Korean *Dendropanax* lacquer was called “hwangchil” in Korea, “koshiabura” in Japan, and “jin-qi” or “huang-qi” in China. Historic documents from Korea, Japan, and China have noted that Korean *Dendropanax* lacquer has been used as a coating to form an excellent cured film, with a brilliant golden yellow color, on woody and metallic substrates (e.g., armor, helmets, arrowheads).¹ Thus, we wanted to determine the most promising methods for using such a coating in a cost-effective manner.

There is scarce or no accumulated information on the chemical analysis of the lacquer components, the optimal curing time or temperature, or the curing mechanism because the coating technology for Korean *Dendropanax* lacquer has been handed down by tradition until now.

Recently, some research has been carried out to review the coating technology of this lacquer. Photooxidation may be one of the most important reactions in the chemistry of Korean *Dendropanax* lacquer, particularly in surface coating technology, where the molecular complex constituting the cured film results from photooxidative polymerization at ambient temperature. Although Korean *Dendropanax* lacquer can air-dry to a thoroughly dry stage to achieve optimal film properties, curing at elevated temperatures may be required because of its long curing time and the

decrease in productivity due to photooxidative polymerization at ambient temperatures. The aim of this study was to determine the curing behavior of this lacquer in an oven-drying system.

Experimental

Korean *Dendropanax* lacquer is the resinous sap from *Dendropanax morbifera* Lev., which is found in the southern part of the Korean peninsula. The impurities in the resinous sap are usually removed with chemical and mechanical methods such as acetone extraction using a screening procedure and concentration using a rotary evaporator under vacuum.

Korean *Dendropanax* lacquer is a viscous, dark yellow solution. The solvent was composed of turpentine, acetone, and diethyl ether (80:10:10wt%). Solvent was added to dilute the lacquer to 10wt% (of the total weight). Its non-volatile content was 55 ± 1 wt%.

To allow the measurement of infrared (IR) spectra, a bar coater (no. 22) was used to apply Korean *Dendropanax* lacquer 0.9 ± 0.1 g to thin aluminum plates ($7.6\text{ cm} \times 2.4\text{ cm} \times 19\mu\text{m}$). Coated aluminum plates were then cured in a drying oven at 80°, 90°, 100°, 110°, or 130°C to a thoroughly dry state. The plates were removed at regular time intervals to determine the curing behaviors by IR spectra.

The components of Korean *Dendropanax* lacquer were separated for identification by a GC-17A gas chromatograph (Shimadzu, Japan) fitted with a Hewlett-Packard HP-5 column (crosslinked 5% diphenyl and 95% methylpolysiloxane, $30\text{ m} \times 0.25\text{ mm} \times 0.25\mu\text{m}$) (Hewlett-Packard, Avondale, PA, USA). The gas chromatograph was interfaced to a QP-5000 mass spectrometer (Shimadzu, Japan, NICEM at Seoul National University). The Korean *Dendropanax* lacquer was dissolved in 99% acetone. The column oven temperature was initially held at 65°C for 3 min and then programmed to increase at 5°C/min to 250°C and then held for 3 min. The injection (splitless) and detector temperatures were 300°C and 280°C, respectively. The

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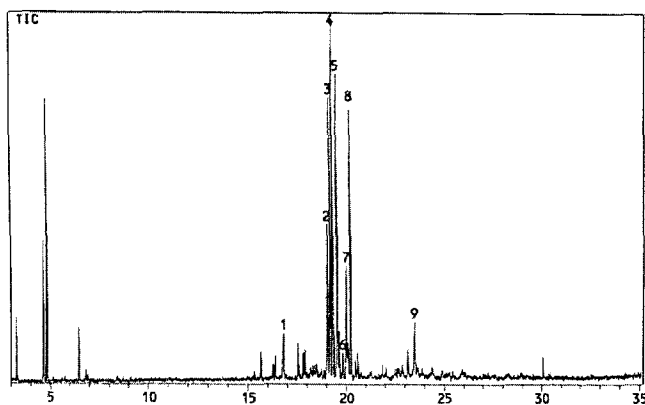


Fig. 1. Gas chromatogram of Korean *Dendropanax* lacquer. (Constituents of the lacquer identified by gas chromatography-mass spectroscopy analysis were 1, β -elemene; 2, copaene; 3, α -cubebene; 4, naphthalene; 5, β -selinene; 6, δ -cadinene; 7, γ -cadinene; 8, β -cadinene; 9, junipene)

carrier gas was helium, with a gas flow of 0.9 ml/min in the column.

The IR spectra were collected using Nicolet Magna 550 series II Fourier transform-infrared (FT-IR) (Midac, Irvine, CA, USA, NICEM at Seoul National University) equipped with the baseline horizontal attenuated total reflectance (ATR) accessory. The ATR crystal material used was zinc selenide (ZnSe), and the resolution of the spectrum was recorded at 4 cm^{-1} .^{2,3} To monitor the curing behaviors and optimal curing conditions of Korean *Dendropanax* lacquer, the stretching vibration peak of the C=C at 1644 cm^{-1} was chosen. The area of the vibration band is calculated using the band in the $1654\text{--}1633\text{ cm}^{-1}$ region, which contains the 1644 cm^{-1} peak. Conversion of the C=C bands, referred to as α throughout the study, was calculated using Eq. (1).

$$\alpha(\%) = \left\{ \frac{A_{T,t} - A_{T,t=0}}{A_{T,t=0}} \right\} \times 100 \quad (1)$$

where A is the area of the vibration band; T is the given curing temperature; $t = 0$ is the initial curing time; and t is the given curing time.

Results and discussion

The gas chromatogram for the Korean *Dendropanax* lacquer is shown in Fig. 1. The constituents of the lacquer analyzed by gas chromatography-mass spectrometry (GC-MS) are given in Fig. 1. The major constituents were naphthanane (21.8%) and β -selinene (19.2%), among others.

The FT-IR spectra of the Korean *Dendropanax* lacquer showed a peak at 1644 cm^{-1} , identified as the C=C stretching vibration. This peak decreases with an increase in the curing time. The decrease of the peak at 1644 cm^{-1} may result from decomposition of the C=C chemical bonds due

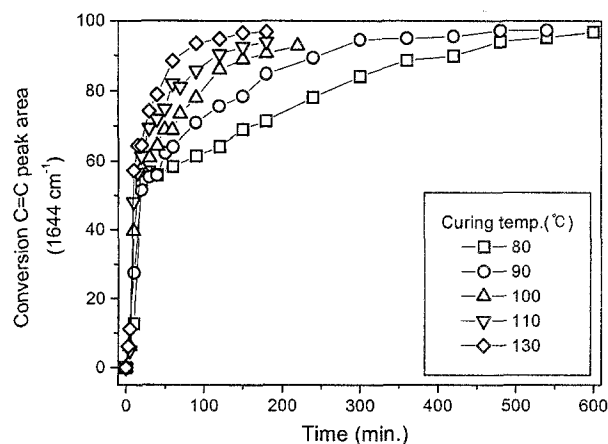


Fig. 2. Change of C=C Fourier transform infrared-attenuated total reflectance peak area at each curing system

to oxidative thermal polymerization of the component.^{4,5} This is made possible by the action of oxygen (oxidation) on the centers of the unsaturation, the reactive sites of the lacquer. Also, there may be migration of double bonds to the conjugated position subsequent to which the conjugated group so formed reacts with a double bond from the lacquer by a Diels-Alder reaction. The polymerization may take place in this manner.⁴ The change in the C=C peak area during the curing process is shown in Fig. 2. The changes in the slope of the C=C peak area depended on the curing temperature, and the slope increased with increases in the curing temperature. Especially, the C=C peak area sharply decreased with increasing curing time up to 30 min, which means a short curing time irrespective of the curing temperature. Changes of the C=C peak area were extremely weak after 150 min at 100°C , after 120 min at 110°C and 130°C , and after 420 min at 80°C and 90°C , with more than about 90% conversion of the C=C peak area.

These results indicate that Korean *Dendropanax* lacquer can be effectively (and economically) cured over 150 min at 100°C or 120 min at 110°C . However, the curing mechanism of Korean *Dendropanax* lacquer requires more detailed research by other methods.

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