

Characteristics of Hardening Behavior of Korean *Rhus* Lacquer by F.T.-I.R.*¹

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F.T.-I.R.에 의한 한국산 옷액의 경화거동 특성*¹

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요 약

한국산 옷액의 경화거동을 알아보기 위하여 F.T.-I.R. 분석을 수행하였다. Acetone 추출한 urushiol의 F.T.-I.R. peak는 3,422cm⁻¹, 2,928cm⁻¹, 1,622cm⁻¹, 1,475cm⁻¹, 1,281cm⁻¹, 984cm⁻¹, 947cm⁻¹, 735cm⁻¹이었다.

또한, 옷액의 경시경화거동에서 1,651cm⁻¹ peak는 urushiol-quinone이 laccase의 촉매작용에 의하여 산화중합한 후 982와 947cm⁻¹의 conjugated diene와 결합해서 dimer 형성을 알 수 있었다.

INTRODUCTION

In some Asian countries, *Rhus* lacquer has been used as a well-known and popular natural coating material for several thousand years. Raw *Rhus* lacquer, the sap obtained from the trees (*Rhus vernicifera* D.C.) of genus *Rhus* that grows mainly in Korea, Japan, and China, consists of acetone-soluble urushiol (60-70%), water (25-30%), acetone-insoluble but water-soluble gummy substances (5-7%), and nitrogen compounds (2-5%) which is insoluble either in acetone or in water.

This raw *Rhus* lacquer is a water-in-oil type emulsion and its main component, urushiol, is dispersed in fine particles surrounded by soluble gummy substances in the aqueous

phase. By exposing to the air, the lacquer changes from milky white to reddish brown in color in several minutes. As the exposing time increase, it becomes more finally hardens to a solid of dark brown color (Kenjo, 1977)⁵.

It is well known that a film of *Rhus* lacquer is formed under the enzymic action of laccase and that has many excellent properties as a natural coating material such as good dispersibility for pigment mixed, good spreadability in painting, the elegant charm and superior indoor weatherability of the coated film on an article, and some flexibility and rigidity imparting high frictional resistance to the coated film despite the well-knit and highly cross-linked structure (Kumanotani et al.

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1968).⁷⁾

Urushiol is a trivial name for 3-substituted alkylcatechols with zero, one, two, and three double bonds in the C₁₅ side-chain, and 8 compounds are identified in the C₁₅ side-chain from the sap of *Rhus vernicifera* D. C. as shown in Fig. 1 (Symes, 1954; Kumanotani, 1983; Du, 1984).^{9),6),2)}

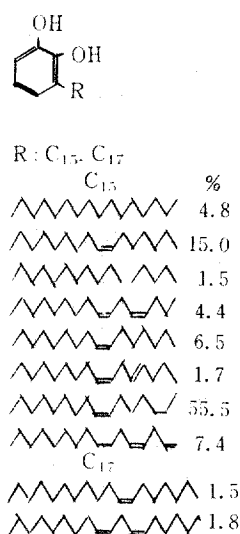


Fig 1. Chemical Composition of urushiol

Most researches on *Rhus* lacquer have been conducted largely in technical aspects in Japan such as painting and decorating, but less studies have been concentrated on the chemical analysis of its components. In earlier studies, the column chromatographic separation of methylated urushiol of Japanese *Rhus* lacquer was reported by Symes et al.(1954).⁹⁾ and the viscoelastic behaviours of raw *Rhus* lacquer and refining process were reported by Amari et al.(1980).¹⁾ Ma et al.(1980)⁸⁾ reported also the separation of 10 μ m ODS-silicagel columns of urushiol in poison and poison ivy. And Yamauchi et al.(1980)¹¹⁾ described that urushiol diacetate was highly resolved according to the dif-

ference in the degree of unsaturation but also in the geometrical and positional structure of its olefinic side-chain through HPLC system. The quantitative composition of the major constituents and the identification of certain minor components in Japanese *Rhus* lacquer have been investigated by Tyman and Matthews(1982).¹⁰⁾ and the identification of constituents and analysis of urushiol in the sap of *Rhus vernicifera* D.C. were carried out by Yumin(1984a, b).^{2),3)}

This paper purposes to present the chemical behaviour of urushiol of Korean *Rhus* lacquer in the enzymic film-forming process related to its structure or the mode of cross-linking in the hardening process, through the analysis of the infrared spectral changes by Fourier Transform infrared spectroscopy.

MATERIALS AND METHODS

The raw *Rhus* lacquer used in this study was obtained from *Rhus vernicifera* D.C. grown in Wonju, Kangwondo, Korea in 1988, and the hardening behaviour characters of the film of *Rhus* lacquer were analyzed by the Fourier Transform infrared spectroscopy. (Model IFS-85, Bruker Co.). Spectra were acquired at a resolution of 4cm⁻¹ by signal 16 scans.

AgBr cell, uniformly coated with the lacquer, was treated at the condition of a temperature 25°C and the relative humidities of 75-85% on a successive time schedules of 0, 30, 60 and 240 minutes, and also 1, 2, 7, 9 and 18 days in humidity chamber.

The film treated on AgBr cell for each fixed time was vacuum dried to eliminate condensed water on the film surface, and then

analyzed by F.T.-I.R. Also, pure urushiol was extracted with acetone from the raw *Rhus* lacquer and analyzed through F.T.-I.R. after vacuum drying for 20 minutes.

RESULTS AND DISCUSSION

The F.T.-I.R. spectra of urushiol, the main constituent of Korean *Rhus* lacquer was shown in Fig. 2.

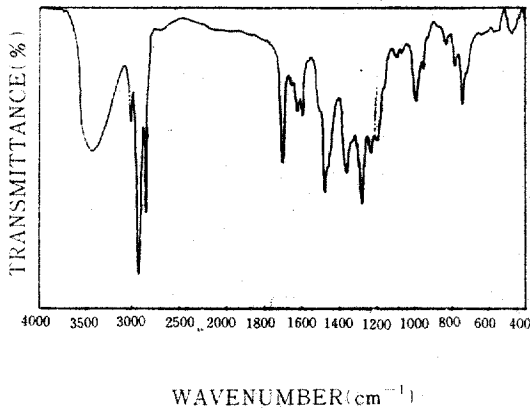


Fig 2. F.T.-I.R. spectra of Urushiol (Wonju)

In the F.T.-I.R. spectra of urushiol extracted with acetone, various peaks were identified as follows: -OH stretching at 3422 cm^{-1} , -CH-CH stretching at 2928 cm^{-1} , residues of *Rhus* lacquer after acetone extraction at 1703 cm^{-1} , C=C of catechol nucleus at 1622 cm^{-1} , C-C at 1475 cm^{-1} , C-O of catechol nucleus at 1281 cm^{-1} , conjugated diene of urushiol side chain both at 984 cm^{-1} and 947 cm^{-1} , and metaposition of urushiol side chain at 735 cm^{-1} .

The peaks shown in Fig. 3 indicate hardening behavior of Korean *Rhus* lacquer films between 800 and 1800 cm^{-1} with the lapse of time.

Absorbance of urushiol-quinone at 1651 cm^{-1} occurred immediately after film appli-

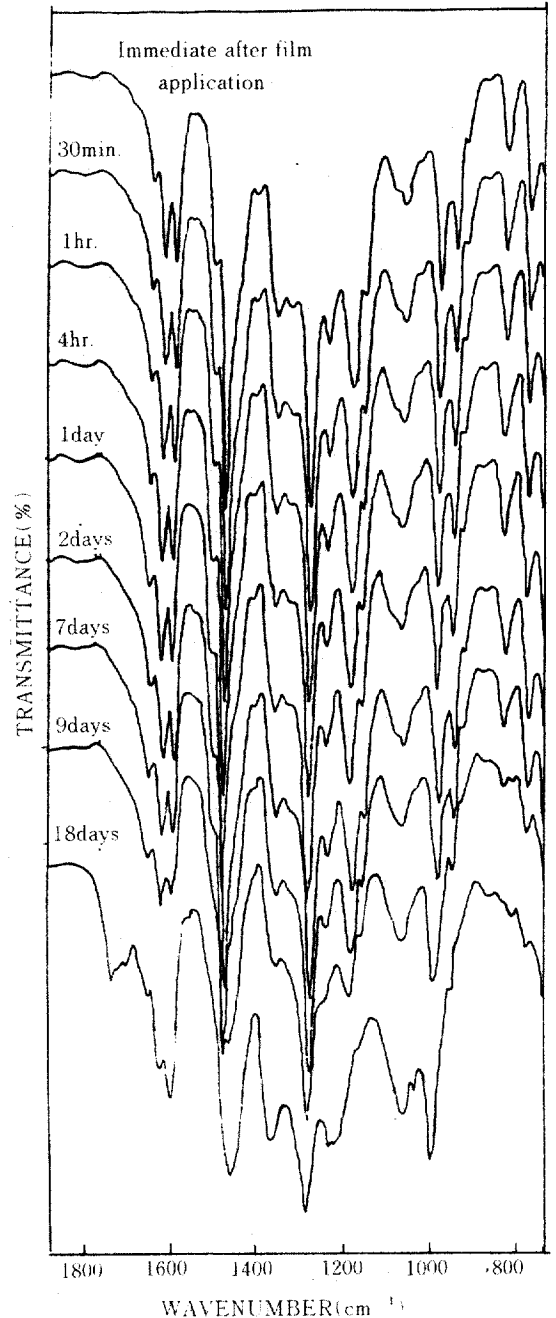


Fig 3. F.T.-I.R. spectra (between 800 and 1800 cm^{-1}) of Korea *Rhus* Lacquer films

cation, which might mean the oxidative-polymerization of urushiol under the catalytic action of laccase and indicated very rapid quinone production. The absorbance at 1651

cm^{-1} was nearly unchangeable by the first day after film application and then increased gradually to maximum peak on the 7th day. Thereafter, this peak decreased slowly and become negligible on the 18th day.

The absorbance of conjugated diene both at 947 cm^{-1} and 982 cm^{-1} immediately after film application decreased remarkably in 9 days and a new absorbance peak of conjugated triene, indicative of dimer II in Fig. 4, appeared at 993 cm^{-1} .

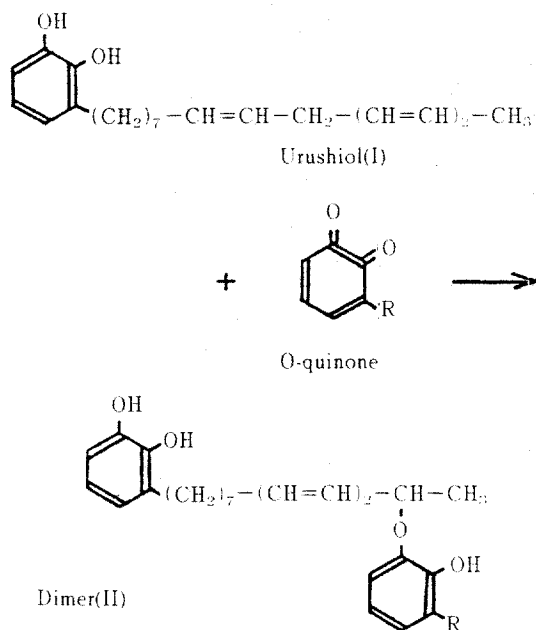
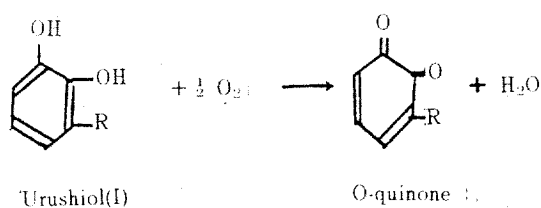


Fig 4. Formation of urushiol dimer

Narrow bands of absorbance at 1595 cm^{-1} and 1622 cm^{-1} occurred by the presence of catechol, not by in-phase skeletal vibration of benzene nucleus. These two narrow peaks re-

mained unchangeable for 7 days after film application and then their peak intensities decreased gradually, suggestive of benzene nucleus combination due to overlap of in-phase skeletal vibration. The absorbances at 1182 cm^{-1} and 1238 cm^{-1} were nearly constant for seven days after film application and then these were began to decrease slowly and finally disappeared on the 18th day, which might be connected with direct bonding of oxygen to benzene nucleus.

The occurrence absorbance at 1738 cm^{-1} , indicative of O-benzoquinone after 18 days from resulted from polymerized quinone compounds and might be related to various carbonyl functional groups formed by oxidation of unsaturated side chains such as α - β diketone and aldehyde.

From the time of film application the sharp and strong absorbance at 1475 cm^{-1} decreased after 9 days and turned into wide absorbance region after 18 days. This wide absorbance region was known to present even after 77 months by Kenzo (1973). The sharp and strong absorbance at 1475 cm^{-1} immediately after film application seems to be caused by bending vibration of CH_2 . And side chains showing absorbance between 1440 - 1465 cm^{-1} in cured film, appear to be caused by active methylene functional group such as $-\text{CH}_2-\text{CO}-$.

CONCLUSIONS

This research was executed to investigate the hardening behavior of Korean *Rhus* lacquer through F.T.-I.R. analysis. The F.T.-I.R. peaks of urushiol extracted with acetone were identified at 3422 cm^{-1} , 2928 cm^{-1} , 1622 cm^{-1} ,

1475 cm^{-1} , 1281 cm^{-1} , 984 cm^{-1} , 947 cm^{-1} , 735 cm^{-1} , in the hardening behaviour with the lapse of time the urushiol-quinone at 1651 cm^{-1} peak, formed by oxidative-polymerization under the catalytic action of laccase, was known to combine with conjugated diene at 982 and 949 cm^{-1} and to form a dimer.

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