

UV-Degradation Chemistry of Oriental Lacquer Coating Containing Hindered Amine Light Stabilizer

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FT-IR/ATR analysis shows that the oriental lacquer coating network degrades mostly in the unsaturated side chain. The rate of increase in carbonyl intensity (a measure of photodegradation) during the accelerated weathering test was substantially different for the unstabilized and stabilized samples; adding 2 wt% HALS into the oriental lacquer formulation enhanced photostabilization up to three times. Weight loss measurements, another indication of photodegradation, and SEM analysis support this conclusion. Despite the presence of the photostabilizer, the other properties of the lacquer were not significantly affected. In particular, the curing behavior of purified lacquer (PL) and HALS-stabilized samples is similar, although the in-situ DETA analysis showed that addition of HALS can slightly retard the cure reaction rate in oriental lacquer coating. It is hypothesized that this cure retardation may be related to the salt formation between HALS and acid of oriental lacquer.

Introduction

Oriental lacquer is a natural product, which has been used for protective and decorative coatings since the second century B.C. The resinous sap was obtained by trapping *Rhus vernicifera* trees. After filtration and traditional purifying, the lacquer can be used directly as a coating material.¹⁻⁸

Although outdoor weatherability is of great importance to the oriental lacquer coating industry, very little is known about the degradation and photostabilization of oriental lacquer. Photostabilization of oriental lacquer can be achieved through a variety of ways, such as pigment addition and the homogenization process.^{9,10} Surprisingly, there is little data on the addition of commercially available photostabilizers in the oriental lacquer coating network. Therefore, it is useful to characterize the curing and weathering properties of oriental lacquer films as well as to study the effect of photostabilization on the physical properties of the lacquer coating network.

As a first step, the effect of weathering exposure on oriental lacquer was characterized through the use of FT-IR/ATR spectra. In an attempt to improve the weatherability of the lacquer, the hindered amine light stabilizer (HALS) and benzotriazole UV absorber were added. To estimate the degree of photostabilization, the surface of the degraded lacquer film was studied by the use of FT-IR/ATR and weight loss determination. The curing behavior and coating properties of oriental lacquer films were also examined.

Experimental Section

Preparation of lacquer films. Chinese raw urushi was filtered using a traditional filter paper called *chilji*. To prepare the purified lacquer (PL, *jungjeotchil*), the filtered raw lacquer was stirred (at 60 rpm) in an open vessel (150 mm(*d*)×150 mm(*h*)) for one hour and then at 45 °C for three hours. The purification procedure for *jungjeotchil* is based on

the traditional method in which the main objective is to reduce water content in raw urushi from 25-35% to 3-6%. The temperature was maintained to sustain the activity level of the enzymes. Three different mixtures were prepared: purified lacquer (PL), PL plus 2% weight hindered amine light stabilizer (HALS), and PL plus 2% weight benzotriazole UV absorber. Both the HALS (Tin292) and the benzotriazole UV absorber (Tin1130) were supplied by CIBA-GEIGY. Each mixture was coated on glass substrate slides (thickness : 60 μm) and was dried for one week at room temperature and at 75±5% RH.

Measurements. The slides coated with the three different films were exposed for 300 hours at 50 °C to continuous irradiation with a UVB-313 lamp in a Q-Pandel Accelerated Weathering Tester (Q-UV). Samples for the FT-IR/ATR measurements were attached to one or both sides of a KRS-5 prism tightly by the use of aluminum foil and silicone rubber. A 45 °C incident light angle was used for the test. In the resulting IR spectra, particular interest was focused on the carbonyl region. The rate of photodegradation of the coating was determined based on measurements of the IR absorbance at 1700 cm⁻¹. The difference spectrum was obtained by using Spectra-Cal software after baseline correction.¹¹ The mass of each sample was measured before and after degradation as a function of photodegradation time. A dielectric analyzer DEA 2970 from TA instruments coupled with a 2100 thermal analyzer was used to obtain the dielectric loss factor for each samples. Parallel plate sensors were used in the dielectric experiments and the dielectric loss factor was measured in the frequency range of 10⁻¹-10⁵ Hz. The surface of the oriental lacquer film samples was investigated through the use of a scanning electron microscope (JSM 840A).

Results and Discussion

The FT-IR/ATR spectra of unexposed and exposed PL

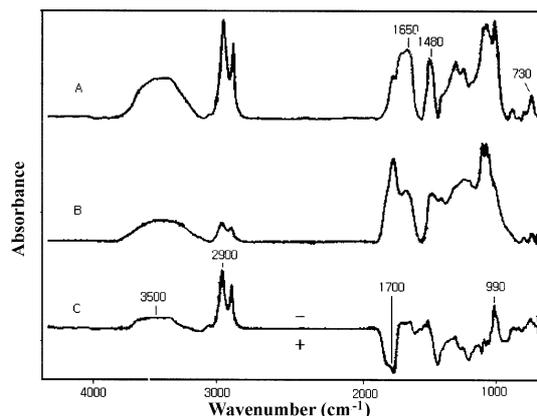


Figure 1. ATR spectra of oriental lacquer film: (a) original; (b) after exposure for 100 h; (c) difference spectrum (a-b).

films are shown in Figure 1. The effect of weathering exposure is more clearly shown in the difference spectrum presented at the bottom of the figure. It is seen that several bands in the spectrum have negative and positive intensities. The presence of the negative and positive intensity bands in the difference spectra can be regarded as resulting from the chemical changes occurring from the photodegradation. The negative absorbance in the difference spectrum reflect the structures that were formed during the photodegradation, and the positive absorbances reflect those structures that were lost. The difference spectrum is dominated by strong bands near 3500, 2900, 1700, 1650, 1480, 990 and 730 cm^{-1} . The broad band near 3500 cm^{-1} was assigned to OH stretching in urushiol. The strong bands related to C-H stretching in the urushiol side chain were observed near 2900 cm^{-1} . The strong bands near 1650 cm^{-1} and 990 cm^{-1} may be related to the C-H out-of-plane bending in the quinone group and in conjugated triene, respectively. The four sets of bands decrease in intensity when the oriental lacquer films are exposed to UV. The band near 1480 cm^{-1} is characteristic of CH_2 bending; its observed decrease in intensity is partly related to decomposition of urushiol side chains. Presumably, the weak peak at 730 cm^{-1} also decreased due to degradation of the aromatic substitute of urushiol. In contrast, the very strong peak near 1700 cm^{-1} increased and was attributed to C=O stretching in the various carbonyl functional groups formed by photooxidation.^{12,13} These results are consistent with the hypothesis that the oriental lacquer coating network degrades mostly in the unsaturated side chains.

These spectral changes can be explained by the photodegradation mechanism suggested as shown in Figure 2. Hydroxy (OH) and hydroperoxide (OOH) groups are formed in reactions between polymer oxy radicals ($\text{PO}\cdot$) and polymer peroxy radicals ($\text{POO}\cdot$) with the same and/or neighboring polymer molecules (RH), respectively. Carbonyl groups of urushiol side chain can also be formed by the internal rearrangement of polymer alkoxy ally biradical leading to the formation of ketones.¹⁴

Since one of the weaknesses in oriental lacquer coating is poor weatherability, the benefit of adding either hindered

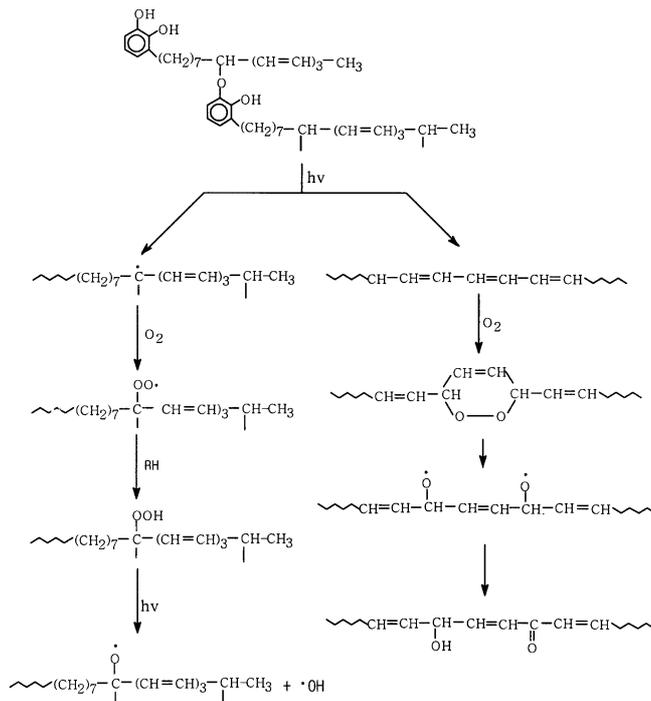


Figure 2. Schematics of the possible photodegradation mechanism for oriental lacquer coating network.

amine light stabilizer or UV absorber to the formulation for photostabilization was investigated.

As a measure of the photodegradation rate, the change of the carbonyl group near 1700 cm^{-1} during photo-oxidative degradation was monitored.¹⁵ In Figure 3, the carbonyl intensity is plotted as a function of UV exposure time. The rate of increase of carbonyl intensity is proportional to the degradation rate.¹⁶ Carbonyl absorbance starts increasing immediately for the unstabilized oriental lacquer film during UV exposure. This behaviour can be explained by the fact

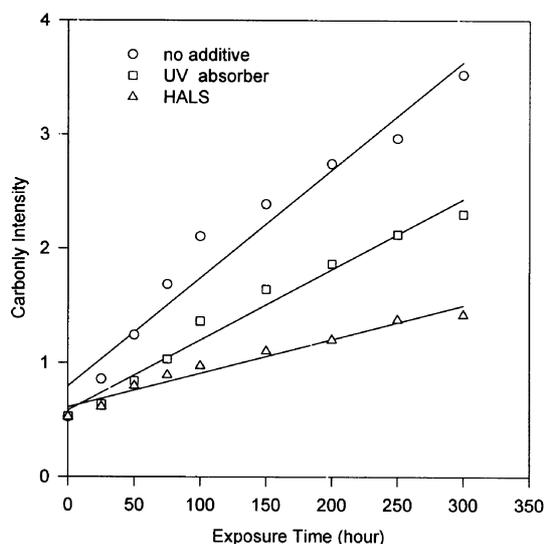


Figure 3. Increase in FT-IR/ATR carbonyl intensity with exposure time.

that a small number of photosensitive groups had already been formed in the lacquer film during the photodegradation processing. The photolysis of these groups gives rise to carbonyl products.¹⁷ The rates of increase of the carbonyl intensity for the photostabilized mixtures are lower than that of the unstabilized mixture. Given its lower rate of carbonyl intensity increase, HALS is more effective than benzotriazole UV absorber in photostabilizing the oriental lacquer system. Adding 2 wt% HALS into the oriental lacquer coating reduces the intensity of the infrared carbonyl band up to three times.

In order to confirm this result, we also measured the weight loss of lacquer film during photodegradation. Although this method may not completely predict the durability, it can be important for a quantitative analysis of the photostabilization effect. Figure 4 shows the weight loss as a function of exposure time. All of the lacquer films lose weight as a result of photodegradation. This may be due to the evaporation of water in oriental lacquer film. However, it is supposed that the weight decrease of the lacquer film is mostly due to the decomposition of polymerized urushiol chains in the surface layer.^{13,18} The slope of the weight loss curve was steeper in film PL than in film containing the photostabilizing additives. The weight loss of lacquer films containing HALS and benzotriazole UV absorber is negligible in the first 50 hours of exposure. After 50 hours of exposure, weight loss starts to occur. Again, HALS appears to be better than UV absorber for the photostabilization of oriental lacquer coating; the rate of weight loss for the HALS-stabilized sample is not as great as the rate for the sample with UV absorber.

The mechanism for this improved photostabilization is not clear yet. It is hypothesized that the photostabilization of HALS in the oriental lacquer film may relate to the nitroxyl radical (NO·), generated by oxidation of the parent amine (NH). The nitroxyl radicals act as efficient radical traps, which may scavenge chain- or chain end-radicals (P·) formed in the photo-oxidative process of oriental lacquer

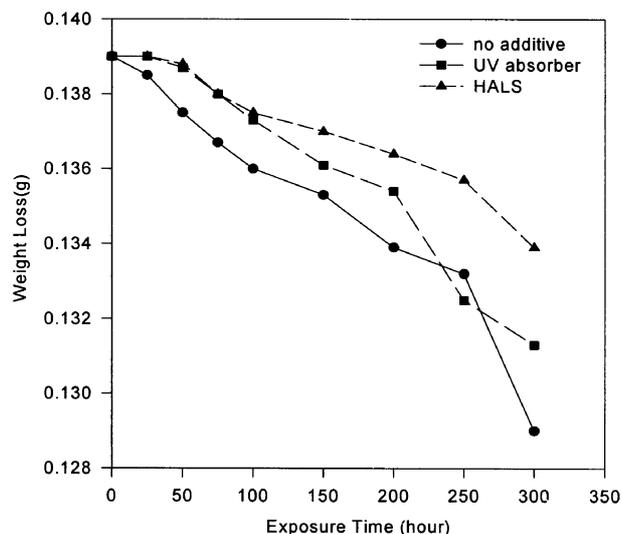


Figure 4. Weight loss of lacquer film with exposure time.

coating to produce substituted hydroxylamine ether (NOP) groups. Further reactions with peroxy radicals (PRO·) regenerate the nitrified groups. All of these reactions effectively terminate free radical chains and reducing oxidation. It can be summarized that the HALS additive in the lacquer film acts primarily as a light-stable antioxidant and its oxidation product function as a free radical scavenger.^{16,19,20}

Scanning electron micrographs (SEM) of the surfaces of the lacquer films are shown in Figures 5-6. The morphology of unexposed and exposed oriental lacquer films is represented in Figure 5. The surface of the unexposed lacquer film has small pin holes of 0.1-2 μm diameter, which is due to polysaccharide particles composed of polymerized urushiol and glycoproteins.⁷ When lacquer films are exposed to UV light, large holes of 10-80 μm diameter appear together with small holes of 0.1-3 μm diameter. The large holes may be formed by the deterioration of the polysaccharide walls and polymerized urushiol.^{7,9} After exposure to UV light, the holes become larger and more numerous. As shown in Figure 6, photodegradation is significantly inhibited by the addition of 2 wt% HALS.

At this point, it is necessary to discuss the effect of adding HALS on the curing and film properties of oriental lacquer. It is worth mentioning that photostabilization of oriental lacquer coating should not cause the deterioration of other important coating properties.

Figure 7 shows the dielectric loss factor measured at a fre-

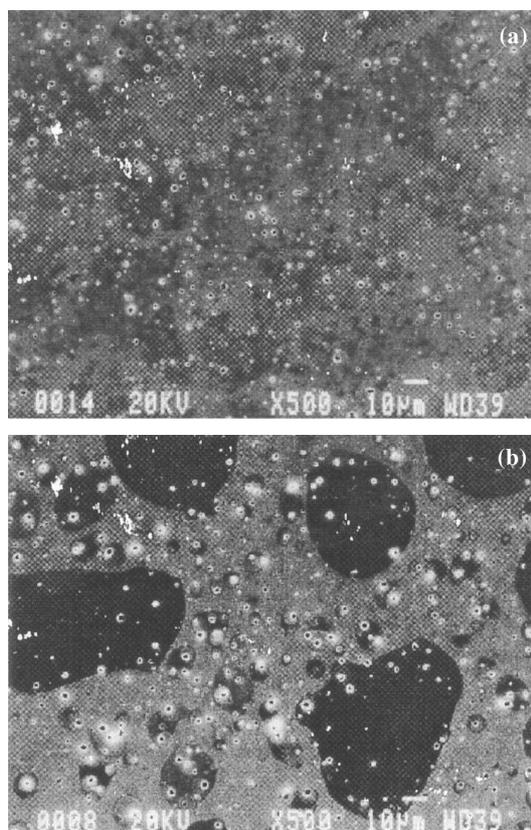


Figure 5. SEM of (a) unexposed lacquer film and (b) exposed lacquer film for 100 h.

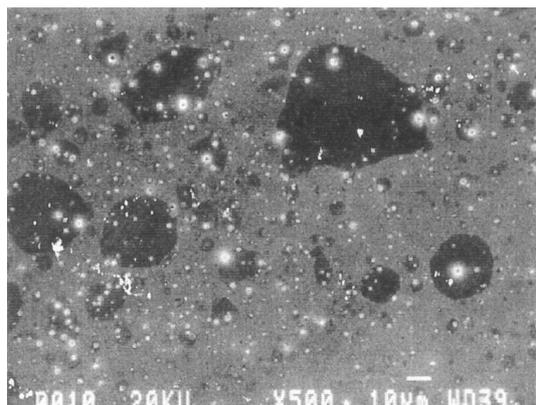


Figure 6. SEM of exposed lacquer film containing 2 wt% HALS for 100 h.

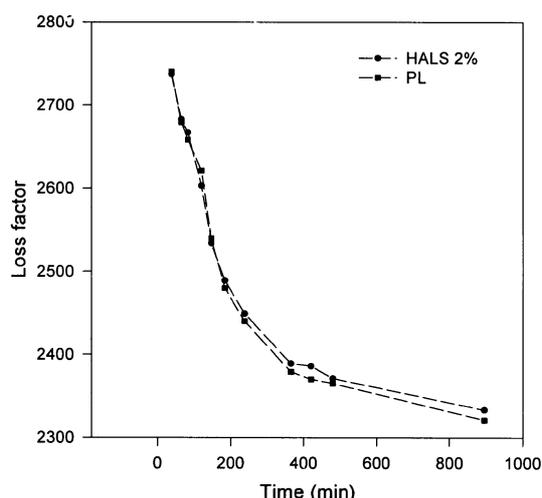


Figure 7. Dielectric loss factor measured at a frequency of 100 Hz plotted against curing time at room temperature.

quency of 100 Hz plotted against curing time at room temperature. The dielectric loss factor is a measure of the cure of the lacquer coating. In the case of PL, the dielectric loss factor decreases with curing time. This decrease may be due to the viscosity increase of oriental lacquer because of crosslinking. The addition of 2 wt% HALS does not change the overall curing pattern of PL, but reduces the curing rate slightly. This may be a result of salt formation between HALS and the acid component of oriental lacquer. Since oriental lacquer cures mostly through enzymic oxidation and the enzyme (laccase) can be active only at acid environment (pH 4-5), basicity of HALS will reduce the curing rate by inactivating enzyme resulted from altered pH value of the

Table 1. Surface properties of oriental lacquer film containing 2 wt% HALS

	Pencil Hardness	Adhesion		Gloss (%)	Contact Angle (degree)
		On Wood	On Glass		
PL	HB	100/100	40/100	62	14
2 wt% HALS	HB	100/100	37/100	60	17

coating.²¹

Finally, general coating properties are compared for the two systems in Table 1. The differences seen in surface free energy and gloss are not significant.

Conclusion

FT-IR/ATR analysis revealed that the oriental lacquer coating network degrades mostly in the unsaturated side chain. FT-IR/ATR results of accelerated weathering test (Q-UV) showed that the addition of 2 wt% HALS into oriental lacquer formulation enhanced photostabilization up to three times. Weight loss measurements, as an indication of photo-degradation, and SEM analysis support this conclusion. Although the curing behavior of PL and HALS-stabilized samples is similar, in-situ DETA analysis shows that addition of HALS can slightly retard the cure reaction rate in oriental lacquer coating. It is hypothesized that this cure retardation may be related to the salt formation between HALS and acid component of oriental lacquer.

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