Development of a Fast Drying Hybrid Lacquer in a Low-Relative-Humidity Environment Based on *Kurome* Lacquer Sap

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ABSTRACT: Hybrid lacquers that dry quickly in a low-relative-humidity environment were synthesized with the repeated *kurome* lacquer process and an organic silicone compound. An investigation by gel permeation chromatography showed that fractions with different molecular weights showed a lower monomer concentration than the pure *kurome* lacquer. Fourier transform infrared spectra of the hybrid lacquers revealed that absorption due to the ether of the quinone olefin and/or dibenzofuran appeared around 1470 and 1080 cm^{-1} and increased with the number of drying days. The gel fractions in the lacquer films increased according to the number of drying days, and this showed that the hybrid lacquers had higher gel fractions than the pure *kurome* lacquer in the initial stage of dryness. In addition, the drying mechanism of the hybrid lacquers was analyzed with an automatic drying time recorder and rigid-body pendulum physical property testing measurements. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1055–1061, 2005

Key words: FTIR; gel permeation chromatography (GPC); hybrid; lacquer

INTRODUCTION

Lacquer sap, which consists of urushiol (60–65%), a gummy substance (5–7%), glycoprotein (2%), and water (20–30%),[1,2] extracted from the lacquer tree in China, Japan, Korea, and other Asian countries, has been used as a coating material for several thousand years.[3,4] A great number of cultural treasures coated with lacquer have been preserved for more than a 1000 years without having lost their original elegant beauty.[5,6] Previously, the partial structure of a polysaccharide in the gummy substance of Chinese lacquer was determined by methylation analysis[7] and nuclear magnetic resonance measurements.[8] The specific biological activities[9] and structure and molecular weight of Asian lacquer polysaccharides have also been investigated.[10] Urushiol is a mixture of many isomers of 1,2,3-tri-*O*- or 1,3-di-*O*-substituted catechols with a long alkyl chain with double bonds.[11,12] Laccase consists of a copper glycoprotein that functions as the polymerization catalyst for urushiol.[13] The lacquer film is formed by the oxidation of urushiol catalyzed by laccase, which is followed by a coupling reaction as well as an autoxidation reaction on the long aliphatic unsaturated side chain. Three kinds of lacquer trees, *Rhus vernicifera* (China, Japan, and Korea), *Rhus succedanea* (Vietnam), and *Melanorrhoea usitate* (Thailand and Cambodia) are grown in the orient.[14] The lacquers are named according to their place of production.[15]

In our previous studies, we successfully developed a small kneading mixer capable of repeated *kurome*, and the drying time of repeated *kurome* lacquers was investigated.[16,17] In addition, as a preliminary experiment, we reported the development of several hybrid lacquers that dry quickly in a low-humidity environment.[18] As part of our ongoing research, in this study, a fast drying lacquer based on repeated *kurome* lacquer was hybridized with various organic silicones, and the characteristics and drying mechanism of the new synthetic lacquer were analyzed in detail.

EXPERIMENTAL

Materials

Raw lacquer from a Chinese lacquer tree at Chengkou in the Hubei Province of China was purchased from Tohityu-Urushi-Ya (Osaka, Japan). Because the raw lacquer had high moisture (20–30%) and the organic silicone was going to be analyzed in water, repeated *kurome* lacquer was used for hybridizing in this test. The repeated *kurome* process was carried out according to a previous method.[18] Twice repeated *kurome*

lacquer (K-2) was used in this study. The moisture concentration of K-2 was about 3.42%.

The organic silicone compounds were purchased from GE-Toshiba, Tiso, and Sinnetsu Silicone Co., Ltd. (Tokyo, Japan).

General

The molecular weight of the hybrid lacquers was determined at 40°C by aqueous-phase gel permeation chromatography [GPC; TSKgel columns α-3000, α-4000, and α-M, ϕ7.8 mm $\times$ 300 mm $\times$ 3, Tosoh; dimethylformamide (DMF) as an eluent with 0.01 mol of LiBr] on a high-performance liquid chromatography system with a refractive-index detector with polystyrene standards having molecular weights of 5.00 $\times 10^2$, 2.63 $\times 10^3$, and 1.81 $\times 10^4$. The elution rate and pressure of the DMF eluent were 0.8 mL/min and 48 kgf/cm², respectively.

The viscosities of the hybrid lacquers were determined at room temperature with a Brookfield Engineering Laboratories, Inc., programmable DV-II+ viscometer. The spindle was a CPE-51, the rotation speed was 5–20 rpm, and the measurement sample was 0.5 mL.

An MX-50 moisture meter (A&D, Co., Ltd., Osaka, Japan) was used to estimate the water concentration of lacquer sap at 110°C. The measurement was repeated five times, and the moisture concentration was calculated by the averaging of the five readings. All substances that evaporated below 110°C were considered moisture.

IR spectra were taken on a Jasco Fourier transform infrared 460$^+$ spectrometer (Tokyo, Japan). Because it was possible for the moisture in the lacquer sap to melt the KBr or NaCl board, a poly(vinylidene chloride) film (Saran Wrap, Asahi Kasei, Japan) was used to make the IR sample. The lacquer sap was thinly applied with a spatula on the poly(vinylidene chloride) film, and the same kind of poly(vinylidene chloride) film was used as a blank.

The drying time of the hybrid lacquers was determined with an automatic drying time recorder (TaiYu Equipment Co., Ltd., Osaka, Japan). The thickness of the tested lacquer films was 76 μm. The lacquer drying process could be divided into three steps: dust-free dry (DF), touch-free dry (TF), and hardened dry (HD).[14] This process could be used with the automatic drying time recorder. The time until the mark of the needle appeared on the glass board was equivalent to DF, the time until the mark of the needle appeared on the lacquer film surface was equivalent to TF, and the time until the mark of the needle disappeared completely on the lacquer film surface was equivalent to HD.

The drying mechanism of the lacquers was measured with a rigid-body pendulum physical property

TABLE I
Distribution of the Molecular Weights (MWs) of the Hybrid Lacquers

Entry	Additive	MW distribution (%)		
		Monomer	Oligomer	Polymer
1	None	59.40	40.04	0.56
2	IPTES	55.78	43.63	0.59
3	APTES	49.65	46.72	3.63
4	BTMSEA	55.62	40.38	4.00
5	AATMS	51.00	42.43	6.57

Polymer: 10000 $\geq$ MW > 3000; oligomer: 3200 $\geq$ MW $\geq$ 640; monomer: MW = 316–320.

testing (RPT) instrument (A&D). A decrease in the cycle length meant that the crosslinkage reaction of urushiol occurred. A steady change in the logarithmic attenuance meant that HD was over. The glass-transition temperature (T_g) of the lacquer films was also analyzed by RPT. The RPT oven was programmed with 0°C as the start temperature, a rise of 2°C/min, and a final temperature of 250°C.

Methods

Repeated *kurome* lacquer K-2 (100 g) was mixed with an organic silicone [X—R—Si—(OCH₃)₃, R = (—CH₂)$_n$—] in different proportions and continuously stirred at room temperature at 250 rpm for 30 min. After storage in a tube for 1 month (room temperature), the characteristics of the hybrid lacquer were tested.

RESULTS AND DISCUSSION

To determine the optimal percentage of the organic silicone compound, we added 1, 3, 5, 7, 10, 20, and 30 wt % organic silicone compound to the *kurome* lacquer sap, and then changes in the molecular weight, viscosities, and drying times of the hybrid lacquers were investigated in detail. The results revealed that a 5 wt % addition of the organic silicone compound produced a suitable viscosity, a good proportion of different molecular weights, and the best drying time in natural and low-humidity environments. In this study, the *kurome* lacquer sap hybridized with 5 wt % silicone was tested.

The percentages of different molecular weights of the hybrid lacquers measured by aqueous-phase GPC are summarized in Table I. Because the addition of silicone was only 5 wt %, the homopolymerization of the silicone compound was disregarded.

After the organic silicone compound (5 wt %) was added to the K-2 lacquer sap, the monomer decreased, and the proportion of oligomers and polymers increased compared with those in K-2 alone; this suggested that a reaction between urushiol and the silicone compound occurred. Silicones with an isocyanet
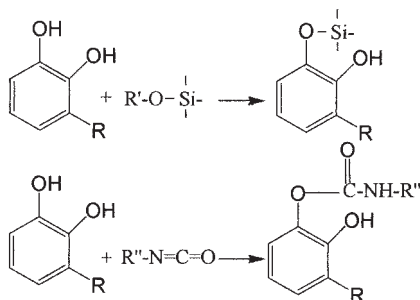
Scheme 1 Reaction between urushiol and Si and isocyanet residue.

Scheme 2 Sol–gel reaction between silicone and water.

residue [3-isocyanatepropyltriethoxysilane (IPTES)] not only reacted with urushiol but also reacted with the hydroxyl group of urushiol through its Si residue,[15,18] as shown in Scheme 1.
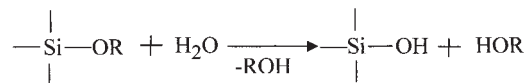
The viscosities of the hybrid lacquer were estimated at room temperature with a Brookfield programmable DV-II+ viscometer. A 0.5-mL sample was used for the test. The spindle was a CPE-51, and the rotation speed was 5–20 rpm. The results are summarized in Table II.

Adding 3-aminopropyltriethoxysilane (APTES) and N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AATMS) increased the viscosities and caused reaction heat to be emitted. This can be considered an intense reaction between the amino residue in the silicone and urushiol. Silica matrix formation was promoted to form a high-molecular-weight polymer. Lacquer sap hybridized with AATMS dried in 30% or higher relative humidity (RH), and the lacquer hybridized with APTES could dry in 50% RH. However, because high-viscosity paint is not suitable for applications, it is necessary to dilute it with an organic solvent to lower the degree of viscosity.

The moisture concentrations of the hybrid lacquer saps are summarized in Table II. The lower moisture concentration of pure *kurome* K-2 is compared with that of the hybrid lacquers, and it can be concluded that part of the free water in the lacquer sap reacted with the organic silicone compound and caused a sol–gel reaction that produced alcohol, as shown in Scheme 2. The volatile alcohol was considered to be moisture in this study, as described in the Experimental section.

The IR spectra of the lacquer dried immediately after application at 20°C and 50% RH for 1 day or several days (figure not shown) showed that the dienes decreased to 982 cm^{-1} and the trienes increased to 993 cm^{-1}. Absorption due to the ether of quinone olefin and/or dibenzofuran appeared around 1470 and 1080 cm^{-1} and increased with the number of drying days; this suggested that the hybridization of the lacquer with the silicone compound caused polymerization to occur.

The drying process of a lacquer film involves the oxidation of the urushiol component by laccase, and the dryness of a lacquered film increases because of the enzyme reaction, which forms a dimer, a trimer, oligomers, and so on.

When the monomer concentration decreases to less than 30%, a bridge construction reaction by automatic oxidation of the unsaturated side chain occurs. This does not increase after the automatic oxidation has occurred in most of the lacquer film. Because the hydroxyl group in the catechol of urushiol acts to prevent automatic oxidation after the hydroxyl group in the catechol of urushiol reacts with the enzyme, the drying process moves to the stage of automatic oxidation, as shown in Schemes 3 and 4.
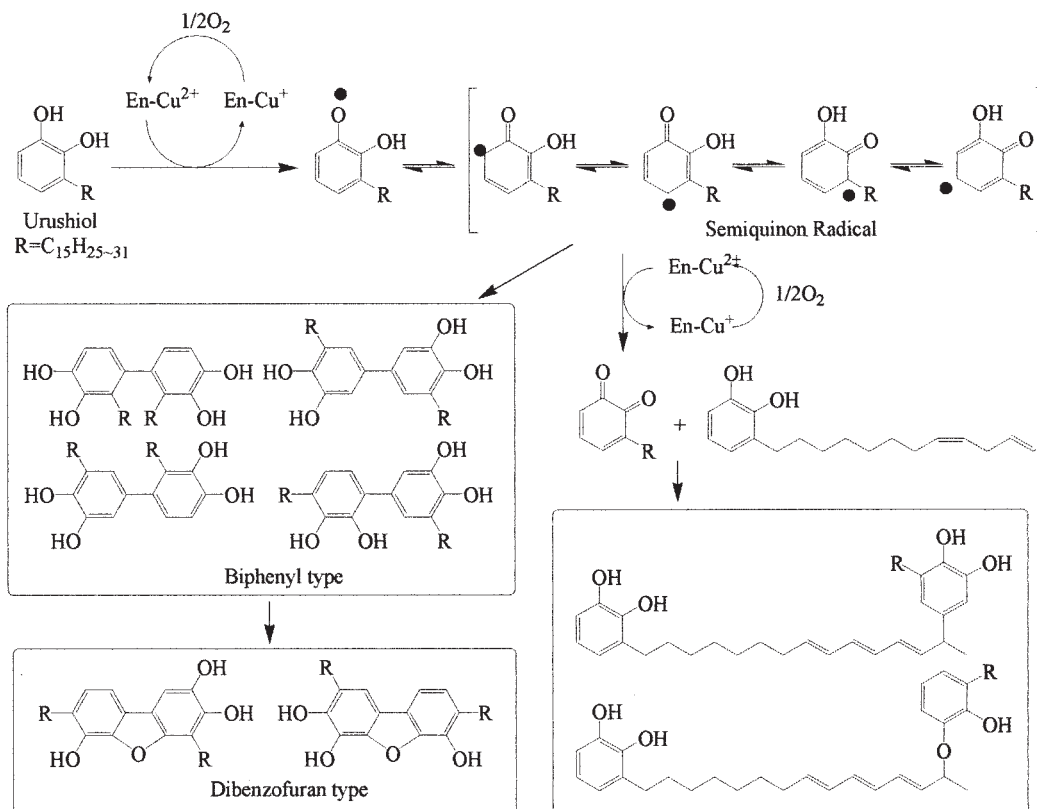
If the proportion of catechol in urushiol decreases in the hybrid lacquer prepared by the addition of an organic silicone compound, the time to automatic oxidation will be shortened, and it is believed that a mass change in a lacquer film will occur earlier. The mass change in the lacquer films was pursued.

The fraction of the gel component in the lacquer films was measured according to the number of drying days, as shown in Figure 1.

The result was that a hybrid lacquer film was obtained to which the silicone coupling agent was added early in the process to change the mass, which decreased; this resulted in automatic oxidation in comparison with additive-free lacquer sap.

The mass reduction of the hybrid lacquer film with APTES and AATMS added was larger than that of other lacquer films. This was presumed to be due to the volatilization of the methanol as the organic silicone compound reacted with the hydroxyl group in the catechol of urushiol and/or the free-water component of the lacquer sap.

The lacquer drying process can be divided into three steps: DF, TF, and HD. The drying times of the hybrid and *kurome* lacquers were tested at 20°C and 30% RH, 20°C and 50–55% RH, and 20°C and 65–70%

TABLE II
Viscosity and Moisture Concentration of the Hybrid Lacquer Saps

Entry	Additive	Viscosity (mPa s)	Moisture
1	None	5,302	3.42
2	IPTES	3,487	4.91
3	APTES	7,180	6.27
4	BTMSEA	4,432	5.84
5	AATMS	26,718	5.78

**Scheme 3** Oxidation of urushiol with laccase.

RH with an automatic drying time recorder. The drying time results are summarized in Table III.

The order of the drying times according to the additive was AATMS, *N,N*-bis-(3-(trimethoxysilyl)-propyl) ethylenediamine (BTMSEA), APTES, and IPTES, in agreement with the viscosity data.

As described in Scheme 1, a sol–gel reaction between the added organic silicone compound and uru-

shiol occurred. The urushiol monomer decreased, and the dimers, trimers, and so forth, the oligomers, and the polymers increased. As the lacquer monomer decreased, the antioxidation of the catechols of urushiol decreased, and the drying time was curtailed.

The measurement of the drying action with an RPT instrument was carried out at 20°C and 55–65% RH, as shown in Figure 2. The frequency decrease means that
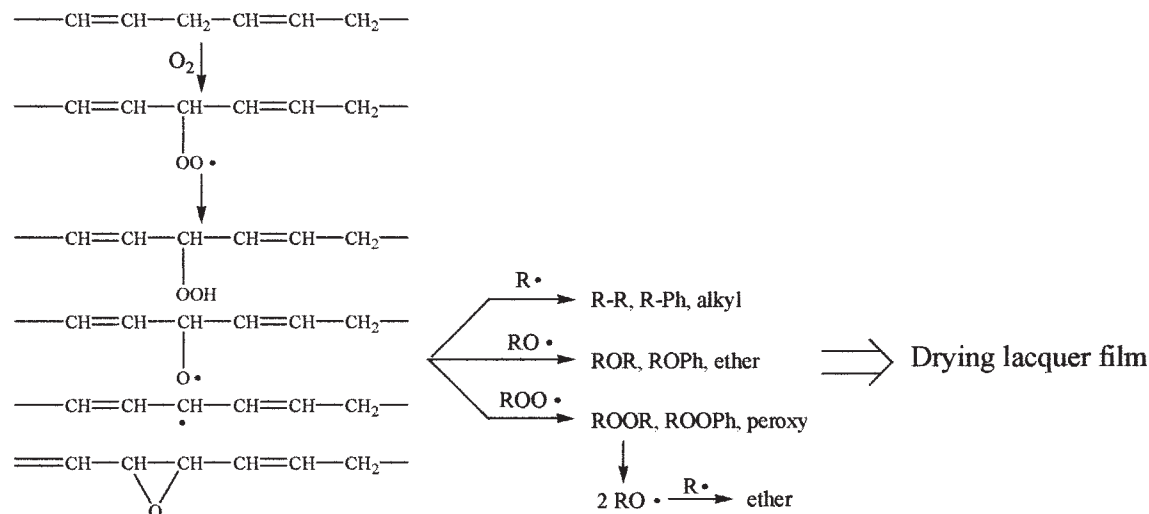
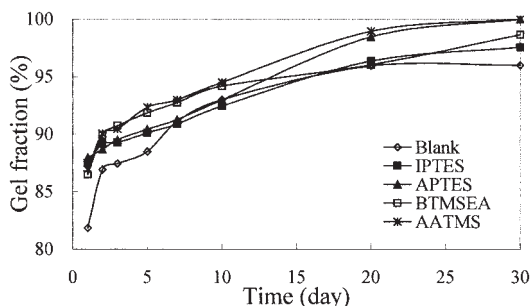**Scheme 4** Autoxidation of an urushiol unsaturated side chain.

Figure 1 Gel fractions of the lacquer films.

I : Blank, II : +IPTES, III : +APTES, IV : +BTMSEA, V : +AATMS

Figure 2 RPT spectra of the blank *kurome* and hybrid lacquers: (A) the frequency and (B) the logarithmic decrement.

the crosslinking reaction of urushiol occurred. A steady change in the logarithmic decrement means that the dry hardening of the lacquer was over. The frequency decrease [Fig. 2(A)], which occurred at 215 min for blank K-2, at 130 min for the IPTES hybrid lacquer, at 85 min for the APTES hybrid lacquer, at 70 min for the BTMSEA hybrid lacquer, and at 55 min for the AATMS hybrid lacquer, was considered to be the transition between DF and TF. The steady state of the logarithmic-decrement values [Fig. 2(B)] of blank K-2 and the IPTES, APTES, BTMSEA, and AATMS hybrid lacquers were 510, 470, 400, 205, and 150 min, respectively, and this was consistent with the HD data in Table III.

T_g of the hybrid lacquer films was also analyzed with the RPT instrument. The hybrid lacquer film dried at 20°C and 60% RH for 1, 3, 8, and 20 days was examined. Figure 3 shows the rheological properties of the samples dried at 20°C and 60% RH for 20 days. The T_g data are summarized in Table IV.

All the hybrid lacquers had a higher T_g than the blank K-2 at any drying time, and the lacquer hybridized with AATMS had the highest. In the initial stage of dryness, the enzyme polymerization reaction played an important role. With the advance of this reaction, the autoxidation of the side chain of urushiol occurred after the urushiol monomer concentration decreased to less than 30%.[19] In the lacquer hybridized with an organic silicone compound, not only the enzyme reaction but also the reaction between urushiol and a silicone compound occurred.[20] Silicones with an isocyanet residue not only react with urushiol but also
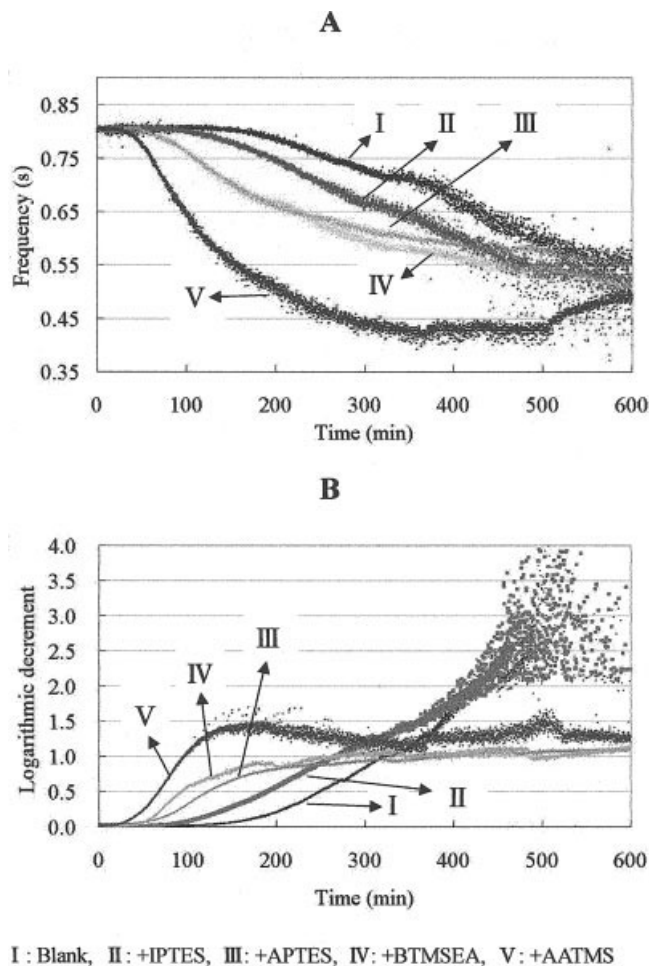
react with the hydroxyl group of urushiol through their Si residue (Scheme 1).[21] As the hydroxyl group in urushiol was consumed, the antioxidization of the urushiol monomer decreased; when the urushiol monomer concentration was less than 30% in the lacquer sap, it initiated the autoxidation of the olefin in the side chain of urushiol and then formed a high polymer. This result shows that the lacquers hybridized with an organic silicone compound not only had an enzyme polymerization reaction (1–7days) but also

TABLE III
Drying Time of the Hybrid and Pure *Kurome* Lacquers

Silicone additive	20°C, 30% RH (days)			20°C, 50–55% RH (h:min)			20°C, 65–70% RH (h:min)		
	DF	TF	HD	DF	TF	HD	DF	TF	HD
None	ND	ND	ND	7:30	12:00	23:40	1:10	2:30	4:20
IPTES	5	30	—	3:00	6:30	10:00	1:30	2:40	3:40
APTES	10	—	—	2:40	5:50	7:30	1:00	2:00	3:20
BTMSEA	5	20	30	2:00	4:30	6:10	1:00	1:40	2:30
AATMS	2	20	30	2:00	4:00	6:00	0:40	1:20	1:50

had an automatic oxidation reaction (>7 days) earlier than K-2.

In general, a lacquer film forms via the oxidation of urushiol catalyzed by laccase, which is then followed by a coupling reaction as well as an autoxidation reaction on the long aliphatic unsaturated side chain, as shown in Schemes 3 and 4.

Urushiol is oxidized by laccase to yield semiquinone radicals, which may undergo reactions in two ways. The semiquinone radical attacks the urushiol nucleus to give biphenyl urushiol, and some of it is converted into dibenzofuran compounds through further laccase-catalyzed oxidation, or the urushiol quinone attacks the unsaturated double bond to form C—C and/or C—O complexes with the side chain; this is followed by H^- abstraction from the methylene group inserted between conjugated diolefins and monoolefins to give a heptatriene cation that may subsequently produce nucleus/side-chain C—C-bond compounds with a conjugated triene structure. The catechol nucleus of the formed urushiol dimers is also susceptible to laccase-catalyzed oxidation to give the corresponding semiquinone radicals, which may behave similarly to the semiquinone radical of urushiol.

Hydroperoxides of the unsaturated side chains may react with the catechol nucleus of urushiol, peroxidase, or metallic ions such as Fe^{2+} (0.05–0.2% Fe is found in a dried film) to give a semiquinone radical or hydroxyl groups on the side chain or cause radical polymerization of unsaturated side chains such as unsaturated fatty oils.

Even though side-chain-oxidized urushiol dimers were separated, urushiol with oxygenated side chains could not be found; this led to the conclusion that side-chain-oxidized urushiol, when it is formed, may be preferentially absorbed on laccase and oxidized to yield dimers. Laccase is a polymeric catalyst, and catalysis may be limited by the mobility of laccase in the polymerizing matrix. When it is immobile, aerobic oxidative crosslinking of the side chains seems to become predominant.
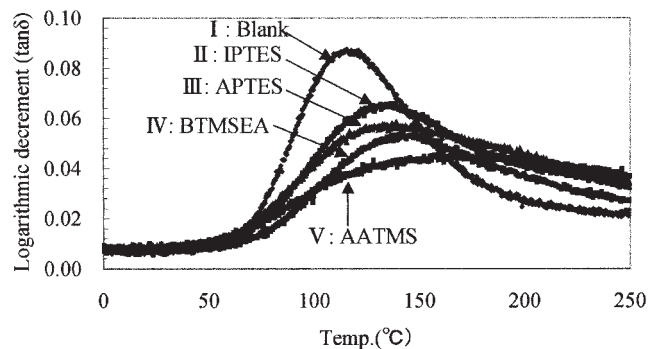
TABLE IV
T_g Values of the Lacquer Films

		T_g			
Entry	Additive	1 day	3 days	8 days	20 days
1	None	47.4	70.0	72.4	120.6
2	IPTES	63.0	71.0	88.2	138.9
3	APTES	81.0	101.9	105.2	142.3
4	BTMSEA	69.0	71.4	77.0	144.1
5	AATMS	125.7	131.9	134.0	170.7

However, in the hybrid lacquer, a reaction between urushiol and the silicone compound occurred. As the hydroxyl group in urushiol was consumed, the antioxidization of urushiol monomers decreased, and the urushiol monomer concentration was then less than 30% of the lacquer sap; this initiated the autoxidation of the olefin in the side chain of urushiol and then formed a high polymer.

The lacquers hybridized with an organic silicone coupling agent with an amine group dried more quickly than the blank lacquer. Although sufficient drying occurred at about 50% RH, an RH environment of about 30% also led to dryness of the formed film with the addition of an organic silicone compound. Because the proportion of polymers increased with the addition of a silicone with an amine residue and the viscosity rose with the generation of heat, a chemical reaction occurred between the lacquer sap and the amine residue, as shown in Scheme 1. A silica matrix formation reaction between silicone and silicone and between silicone and urushiol occurred. Thus, the enzyme oxidation reaction and automatic oxidation reaction of the lacquer clearly coexist during the drying progress of the hybrid lacquer.

Lacquer has had applications only in crafts until now because it requires a fixed temperature and about 70–80% RH and, therefore, requires a special humidity chamber for drying. However, the reaction between urushiol and the silicone compound occurred at a low humidity. The enzyme oxidation, automatic oxidation, and silicone compound reaction that the hybrid lacquer underwent in this study demonstrate that it is possible to dry it in a low-RH environment. Further detailed studies on a hybrid lacquer that is hybridized with two or more kinds of silicone compounds are currently underway.

Figure 3 T_g measurements in RPT of the lacquer film dryness at 20°C and 60% RH for 20 days.

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