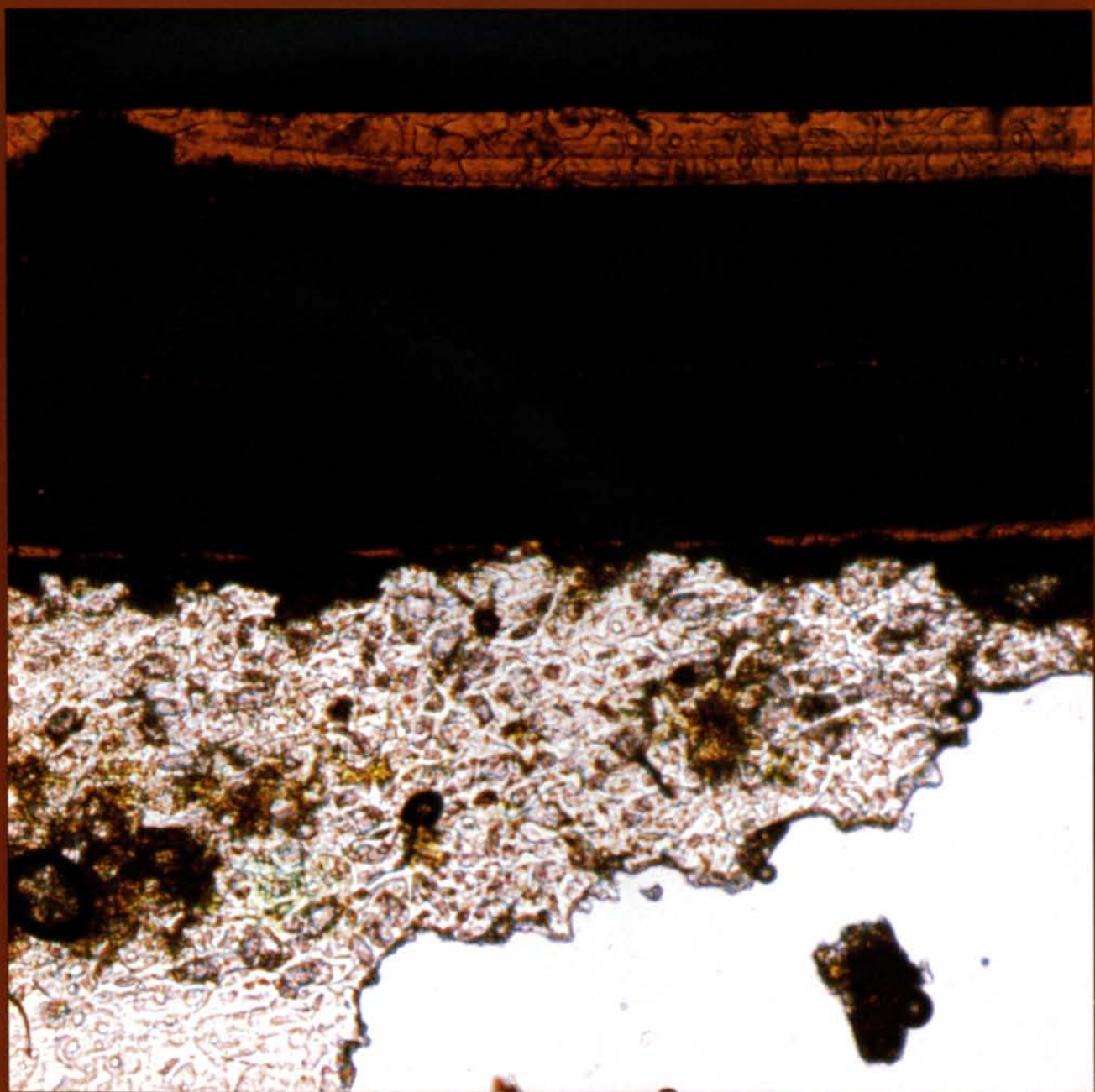


*Photomicrograph (x16) of thin section of Chinese lacquerware object, fifteenth century.*





# Scientific Approach to Traditional Lacquer Art

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Traditionally, lacquering techniques have been handed down from fathers to their sons and from the sons to their own sons, and so on—knowledge gained from accumulated experience. However, the scientific basis for these techniques has never been clarified. After World War II, the old apprentice system was abolished and the duration of training was considerably shortened. This interrupted the traditional passage of lacquer art from father to son. As a result, young lacquer workers today are likely to seek new materials and, particularly, there seems to be some confusion in the handling and evaluation of “good” vs. “bad” urushi. Consequently, to enable us to preserve the traditional art of lacquering for the future, I attempted a scientific study.

At the beginning of the study, I visited some skillful *urushikaki* (sap collectors) and lacquer artists to hear about ways of collecting the sap of the lacquer tree and applying urushi. Then I tried some fundamental experiments to explore the scientific significance of their techniques.

## **Time of collecting and properties of the sap**



Figure 1. Urushi sap immediately after collection (*hatsu urushi*).

The best time for the first incision to collect the sap is said to be about fifty-five days after the cherry trees have blossomed, when the lacquer trees are in full bloom. The sap collected from the first six incisions is called *hatsu urushi*; during July and August it is called *sakari urushi*, and in September it is called *ura urushi*. These terms mean the first-, peak-, and last-collected sap respectively.

Since the sap produces bubbles on its surface, it is covered with a sheet of *shibugami* (Japanese paper) and stored in a cool, dark place; the foam collected on the paper is removed every day. As time passes, the foam gradually reduces in volume and the sap changes from milky-white to a lighter color. The top layer is the most transparent (like seed oil) and brown sediments settle on the bottom of the container. This condition is called *shusse-shita* (matured) by the sap collectors. The sap requires about one month to reach this stage.

The specimen of *hatsu urushi* that we received for study in our laboratory was whiter than we had ever seen before, of very low viscosity, and had a small amount of transparent liquid at the bottom of the test tube (Fig. 1). As soon as the cap was loosened, it popped off and the liquid foamed out. We assume that such copious foam was caused by the high activity of the enzyme in the sap; this was subsequently proved by measurement using the triethanolamine method. As expected, the enzyme activity proved to be much higher than in ordinary raw urushi, i.e., matured urushi sap.

**Table 1. Analysis of urushi**

	Date	Water content	Urushiol	Gummy matter	Nitrogenous compounds	
1984 immediately after collection	July 31	40.98	47.56	9.20	2.26	<i>Sakari urushi</i>
	Aug. 31	26.92	63.65	7.29	2.14	<i>Sakari urushi</i>
	Sept. 24	34.29	56.32	7.61	1.78	<i>Ura urushi</i>
	Oct. 4	34.20	54.25	8.99	2.60	<i>Ura urushi</i>
	Oct. 28	49.35	39.31	9.88	1.64	<i>Ura urushi</i>
1985 approximately one year after collection	May 20	23.80	67.15	6.60	2.45	<i>Hatsu urushi</i>
	May 11	20.11	70.74	5.70	2.45	<i>Sakari urushi</i>

Immediately after collection the sap has a 27–50% water content (Table 1), indicating a different balance of water, nitrogenous compounds, and gummy matter as compared with ordinary raw urushi; about a year after collection it shows a similar composition to ordinary raw urushi. This aging is one of the most important things to be considered in traditional lacquering techniques. Both *hatsu urushi* and *sakari urushi* are low in viscosity at first; as time elapses, white precipitates and a transparent aqueous phase are deposited on the bottom of the test tube. The milky white fraction left in the upper part of the tube increases in viscosity. At about the same time the enzyme becomes less active: no foam is produced but tiny bubbles are seen moving about in the milky white sap.

High performance liquid chromatography (HPLC) of the sap immediately after it was received, when it was producing copious foam, showed only one peak (attributed to urushiol), but as time passed several additional peaks appeared. These peaks are believed to be attributable to urushiol dimers or trimers formed as a result of the oxidative polymerization of urushiol.

The pH of the sap immediately after collection was about 6.0 for *hatsu urushi* and about 5.5 for *sakari urushi*. Both figures have a tendency to decrease with time. Ordinary raw urushi has a pH of about 4.5. It is said that the optimal pH value for enzyme activity is between 5.6 and 6.8. High pH values of the sap in its early stages can be considered important for the maturing of the sap rather than for the hardening of urushi.

From the fact that the sap contained a large amount of water immediately after collection, it was supposed that the aqueous phase might constitute the external phase. To test this, a mixture of water-soluble yellow dye and oil-soluble blue dye was added to the sap. As expected, the external phase was tinted yellow and the internal phase blue, indicating the external aqueous and internal oily phases as shown in Figure 2.

With higher magnification, the internal blue region was found to contain a dispersion of small yellow particles (Fig. 3). Thus the sap of the lacquer tree immediately after collection is a double emulsion of water/urushiol/water.

In actual practice, the sap collected is put into a wooden bucket with a lid; the foam that collects on the *shibugami* (Japanese paper) cover is removed daily (a process called *awa keshi*). Although *awa keshi* seems trivial, it is very important because during the short time of disengaging the cover and removing the foam, the sap is exposed to air and gradually matures into raw urushi.

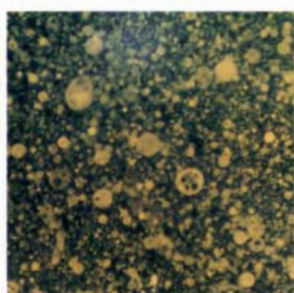
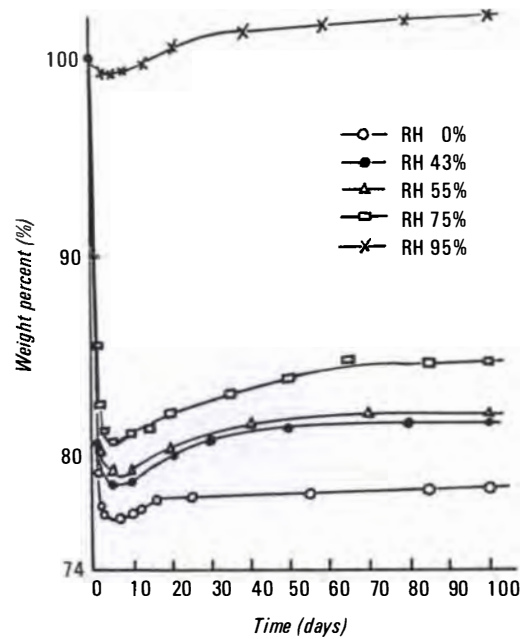


Figure 2. Photomicrograph of urushi sap (40x).

Figure 3. Photomicrograph at higher magnification of the internal phase of Figure 2.

Figure 4. Changes in weight of lacquer film with time.



### Hardening of raw urushi and its use as an adhesive

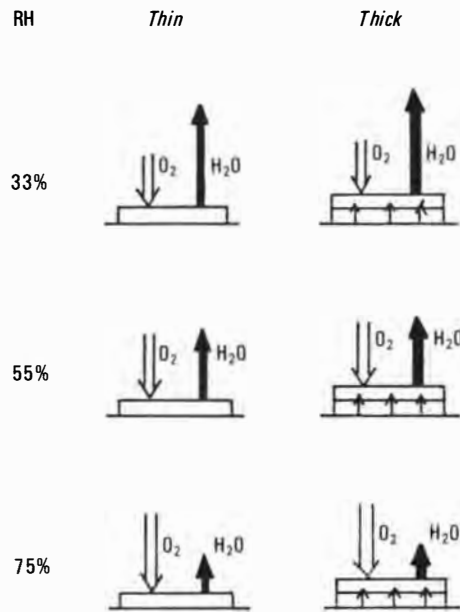
Water content and the ambient relative humidity have a considerable effect on the hardening of raw urushi. The polymerization and hardening of raw urushi at an early stage proceeds with the aid of the enzyme it contains, in direct proportion to the amount of water.

Generally, raw urushi is used as an adhesive for *shitajigatame* (ground consolidation). Raw urushi can form a hardened film varying in appearance and properties according to the ambient relative humidity. The higher the RH, the more opaque and darker the film. Below 55% RH the film is more transparent and lighter brown and has a smooth surface. Figure 4 shows the change in the weight of raw urushi films with time, exposed to several different relative humidities. The weight decreases first at all levels of RH, reaches a minimum, and then increases. The minimum value is reached generally between the fourth and the seventh day. In our experiment, one hundred days after the application of the urushi, when the films were considered to have absorbed almost the maximum amount of oxygen and when the water content had reached equilibrium with the surrounding atmosphere, the water content of the films was determined by drying them at 105°C to constant weight. Water content thus obtained is shown in Table 2, which also shows the hardening time and the appearance of the films. Films having water content below 1.5%, corresponding to those hardened at relative humidities below 55%, are transparent and light brown in appearance. However, at relative humidities below 33%, the films cannot harden completely. Depending on the water content, it can reasonably be assumed that a relative humidity of about 55% will allow a film to harden to “tack free” in a period of one day.

Table 2. “Tack free” time, appearance and water content of urushi films

Relative humidity %	“Tack free” time hr	Appearance of film		Water content of dried film g(H <sub>2</sub> O)/100g
		Color	Gloss	
33	72	Brown	+	1.10
55	24	Brown	+	1.49
75	17	Dark brown	-	4.07
95	15	Dark brown	-	22.60

Figure 5. Changes in oxygen and water contents of thin and thick urushi films at three different relative humidities.



As shown in Figure 5, water evaporates more rapidly from the surface of an urushi film at a low RH than at a high one. With a thick film, at the lower relative humidity of 33%, there is a greater gradient of water concentration leading to faster diffusion of water towards the surface, so the water concentration in the film becomes uniform more quickly. However, because the water content of the film is lower, the film absorbs oxygen more slowly, thus causing slower hardening. On the other hand, at a higher relative humidity (75%), water evaporates so slowly from the surface of the film that the gradient of water content is much less, making water diffuse more slowly in the film. As a result, because of its high water content, the film absorbs oxygen faster, resulting in an opaque, nonuniformly hardened film, with a significant amount of water remaining. At an intermediate relative humidity of 55%, the rate of water evaporation from the surface harmonizes well with the hardening rate (i.e., the oxygen-absorbing rate) to form a uniform, transparent, light-brown, hardened film in a reasonable period of time, about twenty-four hours.

When the film is thin enough to disregard the question of water diffusion within it, the hardening of urushi depends only on the amount of moisture in the environment: the higher the relative humidity, the quicker the rate of hardening. However, since water remains in the film, the latter will become opaque. To keep the film as thin as possible while preventing it from becoming opaque, it is necessary to place it in an environment with higher relative humidity than for a thick film, but not too high. For example, if a thick urushi film hardens in a given length of time at 55% RH, it will be necessary to keep a thin film at 75% RH for it to harden in the same time. It is important to realize that a thin film will harden more slowly than a thick one and therefore require a higher relative humidity if it is to harden in a reasonable period of time. To make a film very hard and smooth like stone, old lacquer artists used to apply many layers of thin urushi at fairly high relative humidity, as in *urushiburo*, a technique for hardening urushi which uses a wooden box (*urushiburo*) kept permanently moist by spraying it with water. This technique can be considered very reasonable from a scientific point of view.

The photomicrograph (Fig. 6) of an urushi film on a wooden substrate hardened at 55% RH shows that the urushi has penetrated into the micella of the wood. However, the urushi film hardened at 75% RH is not uniform and the film hardens so fast that there is no penetration of urushi into the micella.

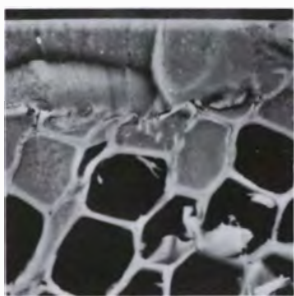
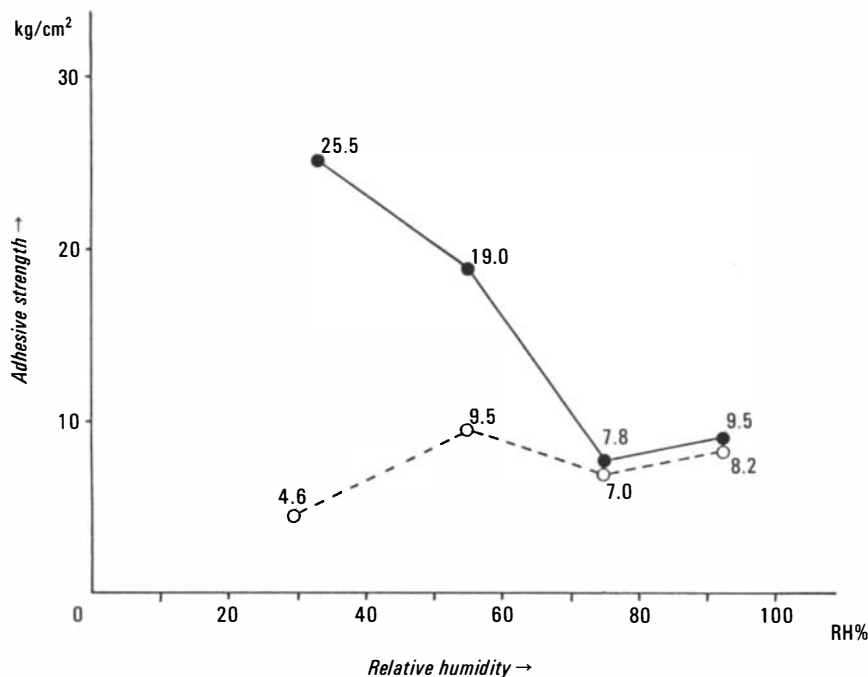


Figure 6. SEM photomicrograph of a hardened urushi film on a wooden substrate (1000x).

Figure 7. Change with time in adhesive strength of urushi films kept at different relative humidities.



The results of measuring the adhesive strength of urushi films hardened at various relative humidities are shown in Figure 7. A comparison of the adhesive strength of the films one month and six months after application shows that it does not change significantly with the lapse of time at higher relative humidities (75% and 92%); however, it increases over time at lower relative humidities (33% and 55%). In particular, at 33% RH, the strength six months after application is five times greater than that one month after application. These results prove the old lacquer artists' saying that the longer the period of time required for hardening, the greater is the adhesive strength obtained.

In order to discover the effect of the water content of the substrate on the hardening of raw urushi, urushi was applied to boards made of Japanese cedar (*Cryptomeria japonica*) and Japanese cypress that had been equilibrated to atmosphere at different relative humidities (92% and 35%, respectively) and kept at various relative humidities (33%, 55%, and 75%). The boards measured 65 x 75 x 5 mm and the thickness of the urushi film was approximately 0.01 mm. On the boards equilibrated at 92% (average moisture content 12.2%), only opaque, dark-brown, hardened urushi films could be obtained, even at the lowest RH (33%), while on the boards equilibrated at 33% RH (average moisture content 7.2%), transparent, light-brown films were obtained at lower relative humidities (33% and 55%). These results show again that moisture content should be kept as low as possible in order to obtain well-hardened urushi films. This generally refers to thick films but, if the time required for hardening is disregarded, well-hardened urushi can always be obtained at the lowest possible RH.

### **Shitajigatame (ground consolidation)**

Japanese traditional lacquering techniques include the *shitajigatame* process, which consists of two subprocesses, *nunokise* and *jigatame*.

*Nunokise* is a process for protecting the substrate and serves as a *komai* (base) for the subsequent process. Cloth is attached to the substrate with *nori-urushi*, a mixture of rice paste and raw urushi. Skillful lacquer artists have told us that rice paste is the best for making *nori-urushi*. The rice paste and raw urushi should be blended until the mixture can be pulled out to make a string about 50 cm long.

Figure 8. Photomicrograph of (a) hemp (200x), (b) flax (200x), (c) ramie (200x).

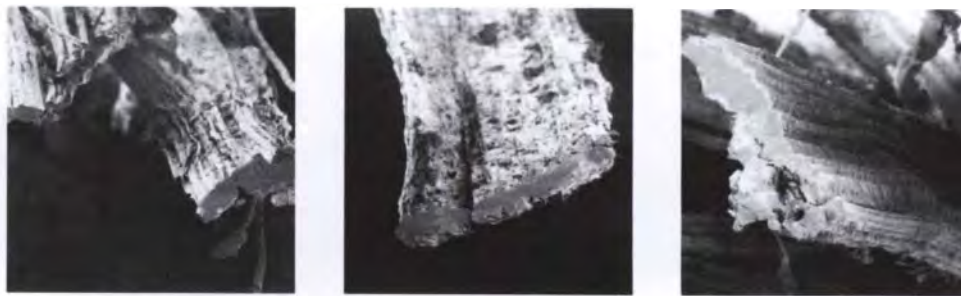


Figure 9. Hemp from makie-bashira in Chusonji temple (300x).

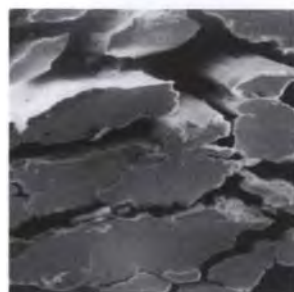


Table 3. Weight gain in saturated water vapor of several fabrics

Sample	Weight of dry sample (g)	Weight gain in saturated water vapor (g)			
		4 hr	8 hr	12 hr	15 hr
Hemp	100	118.3	130.1	142.3	148.7
Flax	100	118.6	129.2	140.8	147.5
Cotton	100	120.3	126.8	136.7	144.5

Table 4. Water and oil absorption of typical clay samples for use in *shitajigatame*

Sample	Water absorption* (g)	Oil absorption* (g)
Wajima-jinoko	8.6	9.8
Yamashina-jinoko	4.5	3.2
Hirasawa-tonoko	5.4	5.1

\*The amount of the vehicle required for the sample to be pasty.

Table 5. Water content at each stage of urushi priming (one week after application)

Relative humidity (%)	Substrate (%)	Solidification (%)	Cloth application (%)	Grounding (%)
55	8.3	8.3	8.5	8.3
75	8.5	10.8	11.9	12.5



Various samples of *nori-urushi*, with different proportions of rice paste and raw urushi, were made and examined in a microscope to assess the blending. The results showed that only the blend with a ratio of six parts rice paste to four parts urushi gave a uniform dispersion. The blend with this critical ratio was also found to have the stringy consistency mentioned above. Due to its water content, the paste accelerates the hardening of the urushi.

Today, hemp, silk, and cotton cloths are used for *nunokise* but it is said that in the old days hemp cloth was mainly used for this purpose. A scanning electron microscope (Figs. 8 a–c and 9) showed the *nunokise* of the *maki-bashira* (a pillar with *makie* decoration) in Chusonji temple to be hemp.

Which is more suitable for *nunokise*, hemp or cotton? Data of absorption and evaporation of water for hemp published by the Sen-i Association (Table 3) show that both rates are greater than for cotton. Therefore hemp sticks to the substrate and also assists the hardening of *nori-urushi* by quickly absorbing excess water from the *nori-urushi* and evaporating it.

In the case of dry lacquer (*kanshitsu*), *nori-urushi* is made by mixing flour into raw urushi, producing what is called *mugi-urushi*. Unlike ordinary *nori-urushi*, in *mugi-urushi* the flour affects the hardening rate of the raw urushi by absorbing water, giving conditions similar to those for hardening at lower relative humidities. Therefore the film hardens more slowly but the hardened film has greater adhesive strength and stiffness than when *nori-urushi* is used.

*Jigatame* serves to protect and thermally insulate wooden substrates. Typical *jinoko* (fired, ground, and screened clays) used for *jigatame* include *Wajima-jinoko* and *Yamashina-jinoko*, named for the places of origin of the clay. Data for water absorption—the amount of water required for making a given *jinoko* paste—are shown in Table 4. This table shows that *Wajima-jinoko* is capable of absorbing a lot of water, so that it requires much more water to make a paste, whereas *Yamashina-jinoko* needs much less water. From photomicrographs of these *jinoko* (Figs. 10, 11) it can be seen that *Wajima-jinoko* contains diatomaceous earth having a porous structure like honeycomb and that *Yamashina-jinoko* is a conventional kind of clay.

Traditional lacquering techniques have skillfully utilized these two kinds of *jinoko*. For example, *Wajima-jinoko* is used by mixing it with rice paste. In this case, the paste serves to accelerate the hardening of the urushi, while the *jinoko* absorbs excess water from the paste to contribute sufficient stiffness and adhesion for the purpose of *jigatame*.

In order to discover the effect of ambient relative humidity on the water content of the material in each *shitajigatame*, wooden boards were subjected to consecutive treatments of *kijigatame* (solidification), *nunokise*, and *jigatame* after having been equilibrated to 55% RH and their water content measured. After each treatment they were kept for one week at 75% and 55% RH and then their water content was measured. The results (Table 5) show that the water content of the substrate kept at 55% RH did not change whereas that kept at 75% RH steadily increased in water content with successive treatments.

From these results it can be seen that the traditional lacquering technique of *shitajigatame* places great emphasis on removing the water content of the urushi film. The technique has been refined in practice, based on the accumulated experience of many artists.

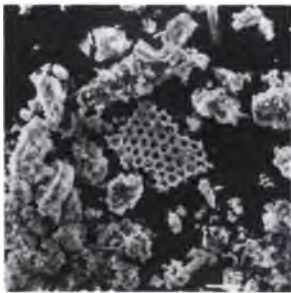


Figure 10. SEM photomicrograph of Wajima-jinoko (1000x).

Figure 11. SEM photomicrograph of Yamashina-jinoko (1000x).

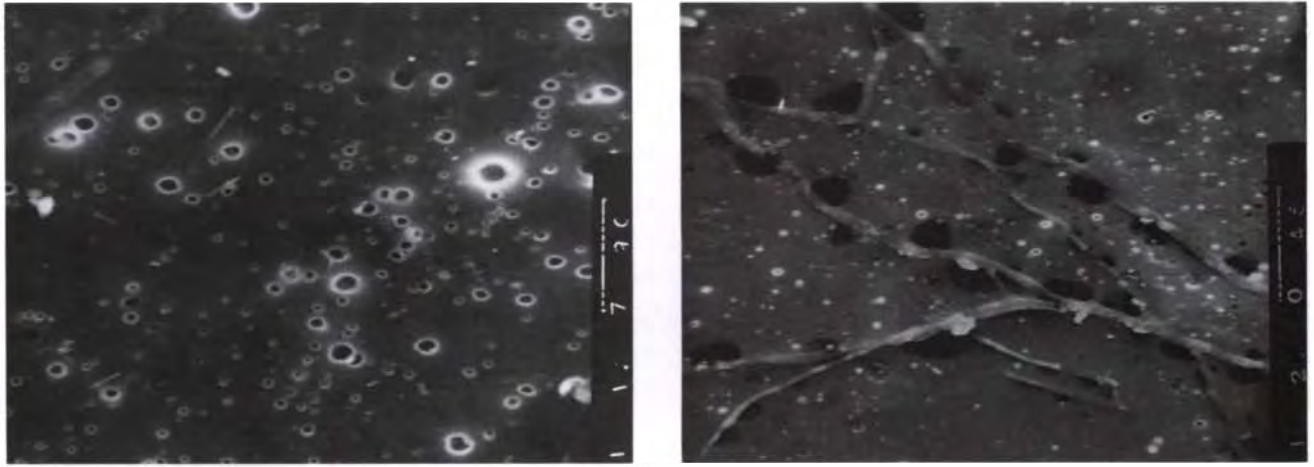


Figure 12. SEM photomicrographs of urushi film after exposure to UV radiation of different wavelengths: (a) 1000x, (b) 3000x.

### **Effect of ultraviolet radiation on hardened urushi films**

Although hardened urushi films are excellent coating materials because they are lustrous and very stiff, their one drawback is that they are sensitive to light, especially ultraviolet radiation. When the film is exposed to UV radiation, part of the polymerized urushiol is decomposed and will volatilize, leaving the film in a heterogeneous condition. A photomicrograph (Fig. 12) of a film exposed to UV shows many black spots surrounded by lighter regions.

Since ultraviolet radiation is very harmful to other works of art besides lacquerware, non-UV fluorescent lamps are now widely used for exhibition purposes.

As a fundamental experiment to discover the effect of non-UV fluorescent lamps, hardened urushi films were exposed to a non-UV fluorescent lamp at several different light levels: 100, 200, 350, and 500 lux for two weeks. Films exposed at 350 and 500 lux showed deterioration similar to that in Figure 12, in which many black spots were seen, whereas those exposed at 100 and 200 lux exhibited no such deterioration. These results show that hardened urushi films are sensitive not only to ultraviolet but also to visible radiation. Therefore, even if non-UV fluorescent lamps are used, works of art, especially lacquerware, should be exhibited below 200 lux and ideally for short periods only.

### **Conclusion**

Japanese traditional lacquering techniques were studied from a scientific point of view. It was found that urushi sap differs in composition depending on the time when it is collected. It is a double emulsion of water in urushiol in water immediately after collection but, as time passes, the water-in-urushiol phase, which is used as ordinary raw urushi, separates from the external aqueous phase. It was also found that oxidation intermediates of urushiol, including urushiol quinone and dimers, which are essential for the hardening of urushi, are formed in raw urushi through a kind of maturing process called *awa keshi*, done by sap collectors during the period of time between collecting the sap and handing over the raw urushi for distribution. This maturing process is important to obtain good urushi films.

In the process of *shitajigatame*, it was found that *nori-urushi* accelerates the hardening of urushi, *mugi-urushi* enhances the adhesion of urushi to the substrate, hemp is used for the quick absorption and desorption of water in *nunokise*, and *jinoko* is utilized to regulate water content. Therefore *shitajigatame*, one of the traditional lacquering techniques, is quite reasonable from a scientific point of view in that it tries to remove as much water as possible from urushi films for their optimal hardening and adhesion.

# Technical Studies of Chinese Lacquer

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Doerner Institut

The title for this article has been chosen both to recall and to extend the work of Sir Harry Garner which was published almost twenty-five years ago. Garner, a collector of Far Eastern art, was the author of several pioneering publications, particularly on Oriental lacquer. He was the first person in the West to employ scientific techniques to try to explain the technical and technological peculiarities of Oriental lacquer. He combined a scientific approach, resulting from his education as a mathematician and astronomer, with a knowledge of Far Eastern art, evidenced both in his publications and by the works of art he donated to the British Museum and to the Victoria and Albert Museum in London. His interdisciplinary interests can be seen in his "Technical studies of Oriental lacquer," published in 1963. He pursued these interests until his death in 1977 and they are found again in the second chapter of his book *Chinese Lacquer* that appeared posthumously in 1979 and that also deals with the technological aspects of urushi.

The beginnings of the present article go back to 1976 and my first thoughts were based on Garner's preliminary work (1963). The aim of these investigations was to find out to what extent scientific examination could help to answer questions of dating, provenance, or identification of Chinese lacquerware. At the same time I intended to extend Garner's work, which concentrates on two pieces from the Ming dynasty (1368–1644), by introducing a series of additional objects to cover a greater timespan, i.e. from Zhou (1027–256 B.C.) to Qing (1644–1912). These investigations and their results are the subject of this article.

## **Garner's literary estate**

It was a happy coincidence that, while a member of the Urushi Study Group in Japan in 1985, I learned that Garner's literary estate was in the possession of the Victoria and Albert Museum in London. Thanks to the generous cooperation of that museum, I was able to study the papers while preparing this article. Garner's papers confirmed that he had tried repeatedly with the help of the natural sciences to solve the technical questions which had occupied him greatly, in and beyond his publications of 1963 and 1979.

At the start of his work there are written notes of his visual appraisal of lacquer objects mainly carved from the sixteenth to eighteenth centuries.<sup>1</sup> The first concrete analytical results soon arrived<sup>2</sup> and are included in Table I of his publication of 1963. They cover not only qualitative but also quantitative emission spectral analyses. Unfortunately, it was difficult to isolate a layer for emission spectroanalysis and so it was necessary to repeat some of the measurements.



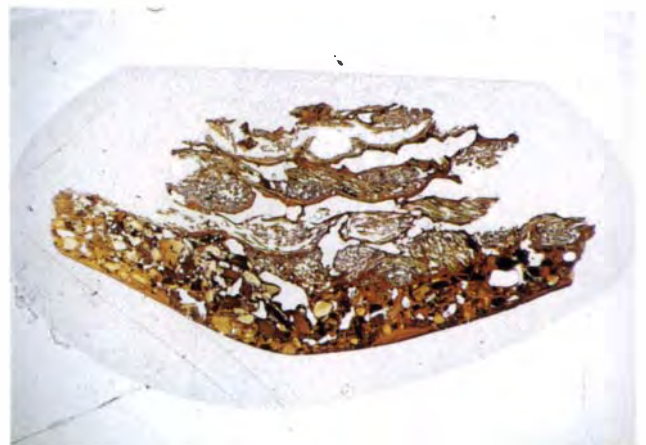
Figure 1. Photomicrograph of a cross section from a Chinese lacquerware object, late sixteenth century, from the estate of Sir Harry Garner (Victoria and Albert Museum, London), taken by A.R. Sollars, Cranfield (magnification x50), supplied with the following commentary on the layer construction: "band 1: 2 layers brownish-red, moderately fine with large inclusions; band 2: 5 layers light red, fine; band 3: 4 layers bright red, coarse; band 4: 1 interface layer, discontinuous, fine layer, grayish; band 5: 1 layer dark gray or black, structureless compared with normal pigmented layers; band 6: 3 brownish-red, similar to band 1; band 7: light red, fine, similar to band 2; and band 8: bright red, coarse as band 3."

At the end of 1962 Garner received five fabric analyses<sup>3</sup> that, together with the cross section and the analyses already mentioned, provided the data for his publication of 1963. This work was received with interest and goodwill.<sup>4</sup> In the same year R.J. Gettens gave Garner additional experimental advice on a piece of carved lacquerware from the late sixteenth century. He recommended the use of a "microscope with vertical illuminator and dark field stop"<sup>5</sup> and magnification of 100–200x. It is interesting that one of the dark layers in this investigation was described as "transparent and non-pigmented." This observation will be discussed later. In reference to the same cross section, A.R. Sollars<sup>6</sup> informed Garner that he had followed the usual procedures for preparing cross sections for microscopy and photomicrographs and that he agreed in general with Gettens' findings. One of the photomicrographs he sent is reproduced here (Fig. 1). This demonstrates the desirability of color photographs for the complex layer construction; Garner's publication (1963) suffers from the absence of color. Apart from these practical issues, Garner was looking for further samples<sup>7</sup> or other analytical procedures. The first attempts to subject urushi to pyrolysis gas chromatography appear to have been successful.<sup>8</sup> Furthermore, scanning electron micrographs increased the knowledge of the pigments used (Hornblower 1962) and Garner received radiographs of earlier lacquerware samples from Gettens.<sup>9</sup> However, Garner also had unanalyzed samples returned to him<sup>10</sup> and these were not the only failures. A manuscript prepared at his suggestion on the chemistry of urushi (Moss 1967) remained unpublished at the request of the author, and many scientists who had hitherto been of great use to him in his research denied him assistance because too great a commitment seemed to be required.

From his correspondence, Garner was also interested in questions of the pigmentation of the black layers,<sup>11</sup> the composition of the black ground used in carved lacquerware,<sup>12</sup> the choice of a suitable method of analysis,<sup>13</sup> correct terminology for the Chinese sources of urushi,<sup>14</sup> the lacquer tree that supplies urushi,<sup>15</sup> and its spread over Asia,<sup>16</sup> and the identification of the fabric support in the lacquerware of the Han era.<sup>17</sup> At the same time he attempted to persuade various colleagues to study a translation he had prepared of the travel diaries of d'Incarville of 1760, which in fact appear to have been one of the most reliable contemporary reports.

Among Garner's papers, evidence can be found of two more experimental initiatives on additional lacquerware. Figure 2 shows the cross section of a carved lacquerware piece that has a construction typical of the Ming dynasty and will be discussed later.<sup>18</sup> A further thin section shows for the first time the construction of a piece from the Han dynasty (206 B.C.–A.D. 220; Fig. 3). It has a thick layer of ground and a thin covering layer over four layers of fabric support.<sup>19</sup>

Figure 2. Fifteenth century, heavy black layer. A new photograph of a thin-section from Garner's estate in transmitted light (16x). From bottom to top: wooden base; heavy black layer (mostly broken away); very thin transparent lacquer layer (looks orange); dark, yellow ground layers; black guide line (Garner 1963) looks transparent orange (see text); red ornamental zone. Figure 3. Thin section of a Han dynasty lacquerware object from Garner's estate.



In order to clear up some misunderstandings and misinformation, we shall start with a discussion of some of the main aspects of debate.

### **Terminology**

The first of these misunderstandings is the question of terminology, to which Garner applied himself in an attempt to discover a common approach in the natural sciences and the humanities to the origins of urushi (Burmester 1985). One glance at this theme in books and catalogs clearly demonstrates the need to establish an agreed terminology.

Identification of the lacquer tree as *Rhus verniciflua* or *Toxicodendron verniciflua* is in keeping with current botanical usage (see note 15; Zander 1972; Hora 1981; Schulze 1966). Hopefully, in the interests of simplicity, *Rhus verniciflua* will be adopted as the exclusive term.

It should be stressed—and this is also clear from Garner's correspondence—that there is no information concerning the spread of *Rhus verniciflua* in the last three or four millenia. Analytical examination of the organic constituents of urushi itself may provide the answer to the question of whether *Rhus verniciflua* has always been the source of raw lacquer. The sap of other trees of the same genus, for example, *Rhus succedanea*, may also have been used.

The extent of the uncertainty about the chemical composition of lacquer can be seen in the range of ambiguous and even false designations that have been used. This is because modern scientific knowledge has hardly ever been applied to the relevant literature. An example of this is the use of the term "urushic acid" (see note 14), meaning the main ingredient of lacquer, which is also called "urushiol." After its first description as "urushic acid" by Yoshida in 1883, it was described as "urushin" and "oxyurushin" in the paper of Tschirch and Stevens in 1905; these authors clearly wanted to demonstrate that the compound in question had nothing to do with acids in the chemical sense. In 1906 Miyama was the first to describe it as a phenol; then finally, in 1908, he used the designation "urushiol." Since then it has been correctly and exclusively referred to in chemical literature as urushiol (for example, Majima 1909). Urushiol is in fact a mixture of phenols and can be taken as a trivial name for an entire group of chemically related compounds.

### **History and technology**

It would appear reasonable to place Oriental lacquer within the range of known binding agents. Urushi can be considered as a colloidal system of a water-in-oil emulsion (Gettens and Stout 1966). Drops of water, containing polysaccharides and an enzyme, are dispersed within an oily phenol phase in which glycoproteins act as emulsifiers (Kumanotani 1979, 1983a, 1983b).

### **Chemical and physical analysis**

As Garner and other scientists have already demonstrated, the natural sciences offer a starting point for the solution of technological problems associated with Oriental lacquerware, although Garner's attempts to analyze the binding agent urushi were not successful. A study of the relevant literature shows that urushi does not form part of the classic analysis of binding agents which is concerned with oils, resins, waxes, gums, proteins, etc.<sup>20</sup> The analysis of urushi—and this is a complicating factor—must take account of its high degree of polymerization and cross-linking, and the addition of inorganic fillers and pigments and organic substances such as drying oils or glues. Although, thanks to the findings of Kumanotani (1979, 1983a, 1983b), our knowledge of freshly polymerized systems is relatively precise, there is no information on the effects of aging. Ideally, urushi should be analyzed after separation into its components; this is always the first step in the analysis of binding agents and

in the case of unhardened urushi. Unfortunately this is prevented by the insolubility of the polymeric system. The limited information supplied by infrared spectroscopy (Kumanotani 1979, 1983a, 1983b; Kenjo 1978) from systems which have not been separated shows that this step cannot be completely ignored. These and other analytical attempts show that our objectives must be modified to pursue analysis "in a quite empirical way, not even identifying components but trying to get distinguishable patterns."<sup>21</sup> Here the possibility of thermal decomposition of the matrix comes to mind. This is achieved by breaking down the polymeric framework and permits analysis of the resulting fragments. But any conclusions about the matrix prior to decomposition still remain problematical.

There is a series of analytical possibilities associated with thermal decomposition of the polymeric framework, which promise to provide more information. The first experiments with pyrolysis gas chromatography carried out for Garner demonstrate this (see note 8). More extensive investigations have shown that pyrolysis mass spectrometry of Oriental lacquer (Burmester 1983a, 1983b), as well as of other natural polymers (Meuzelaar 1982), promises to produce interesting results. However, an interpretation is difficult beyond the level of accepting the results of analysis as a pattern. The introduction of multi-variable statistical evaluation has made progress in pattern recognition (Burmester 1983a, 1983b) but, without extensive preparatory investigations, comparative studies and relevant experience, the results must be treated with caution.

Along with the results already published, limited conclusions may be drawn from the mechanism and regularities of decay of the lacquer sample from its pyrolytic fingerprint in low resolution mass spectrometry (Burmester 1982, 1983c). In relation to questions posed by Garner, some interesting conclusions can be drawn from this experimental starting point. For example, the decomposition of urushi in the case of post-Tang (after A.D. 906) specimens seems to be very well defined. The expected decomposition pattern (Occolowitz 1964) is found in each of the pyrolysis mass spectra, but only in samples of similar age. This is in contrast to earlier lacquerware samples which obviously decompose in a much less defined manner.<sup>22</sup> This may be due to alteration resulting from aging of the lacquer matrix or because the matrix was never structured in the same way as that of more recent carved lacquerwork. This immediately raises the question of whether a different method for preparation of urushi from *Rhus verniciflua* (*kurome* or *nayashi*) was used in earlier times or, indeed, whether another latex was used.

A more precise evaluation of the results can be achieved by improving the system of analysis (a switch from low- to high-resolution mass spectrometry). Computer-supported interpretation of these experimental results permits the identification of individual pyrolysis or ionization products which, in turn, in individual cases, give a clue as to the matrix before thermal decomposition. The experimental conditions for high-resolution mass spectrometry are similar to those already published for low resolution (Burmester 1983b). In order to establish results from this series of measurements on the same basis as those of previous investigations, measurements of samples already published were repeated (Burmester 1983b). The dates of the twenty-six samples, all from lacquer objects of the Linden-Museum (Stuttgart, German Federal Republic), ranged from Zhou to Qing and included a few modern ones. The information obtained so far is summarized.

If the high intensity peaks are filtered out from the mass spectra and related to the most probable combination of elements according to their mass (in this case only C, H, O) it is apparent that certain fragments<sup>23</sup> can be observed in each of the samples investigated. These appear to be quasi "index fossils" that should permit recognition of urushi as a binding agent. As a limiting factor, I must admit that I had no opportunity to examine other saps of the genus *Rhus*.

It is striking that pre-Tang (before A.D. 618) specimens have a substantially higher proportion of carbohydrates (fragments of type  $C_xH_y$ ), while later samples comprise primarily oxygen-containing fragments (of the type  $C_xH_yO_z$ ). This supports the differences already mentioned in lacquerware according to its age.<sup>24</sup>

### **Technological examination of Chinese lacquerware**

In this section the construction of lacquerware is examined with the help of cross sections, and an attempt is made to determine the pigments used. Garner's publication of 1963 was a pioneering work on both of these points. However, the scope has been greatly increased in the present work.

I am indebted to the Linden-Museum, for generously allowing me to examine an extensive group of Chinese lacquerware as well as many pieces of carved lacquer. All the pieces investigated belong to this museum; they were purchased from the Fritz Löw-Beer Collection in 1978 (Burmester and Brandt 1982, Brandt 1982, 1986). The extensive scientific research project examined over forty objects, twenty-eight of which are presented here (Burmester and Brandt 1982).

#### **Methodology**

Small samples were taken from all the objects for the preparation of cross sections. By using laser microanalysis (Moenke, 1968; Roy 1979; Schrön 1983) it was possible to obtain an overall view of the pattern of elements detectable in the individual layers.<sup>25</sup> In this way it was possible to avoid the difficulty, to which Garner referred, of preparing single layers for analysis. In association with microscopic evaluation of the cross sections<sup>26</sup> it was possible to obtain an indication of the pigments used. Parts of the lacquer samples were pulverized for further investigation using mass spectrometry and x-ray diffraction analysis.<sup>27</sup> Here, both Debye-Scherrer and vertical goniometric diffractograms were taken.<sup>28</sup> Under suitable conditions, it was possible to identify the pigments used.

The Appendix contains the results obtained: the macroscopic construction of the pieces, the function of the individual layers, and their pigmentation. In keeping with Garner's method (1963), also reproduced along with the description of the object is the sequence of bands and layers,<sup>29</sup> the color of the bands and their probable function, their approximate thickness (measured from the cross sections) and the pattern of elements obtained by laser microanalysis.

### **Early Chinese lacquerware between Zhou and Song**

The group of early painted lacquerware pieces under investigation includes objects from the Zhou dynasty (nos. 1–5, see Appendix), the Han dynasty (nos. 6–10), the Tang dynasty (A.D. 618–906; nos. 11, 12), and the Song dynasty (no. 13; see also Figs. 4–18). These objects are discussed later in relation to their construction and function and also, in association with carved lacquerware, their pigmentation.

Most of the early painted lacquerware objects have a simple construction. In the case of object No. 1 from the Zhou era (Figs. 4,5) there is only one layer, which is considerably darkened on the surface, over a very thin ground layer. It is very difficult to determine if this was applied on purpose or whether, as has been observed in other cases, it results from residues of abrasives used.

The construction of the objects from the late Zhou and Han eras onwards can be schematized as follows: a ground mixed with coarse minerals (mostly with black additives), followed by one or more covering layers, and on the surface an ornamental, colored layer, usually red or black (Figs. 7,9,11,12,13,15). It is striking that none of the pieces under discussion display any evidence on the surface of the layers of having been worked upon. This indicates that after the drying process the films of lacquer were not rubbed down with abrasives. Plant fibers are often found in the individual layers (Fig. 5, yellow layer; Fig. 7, layer over the black ground). This suggests that the urushi was not filtered.

All the black grounds contain traces of minerals. Laser microanalysis has detected high intensities of silicon, calcium, iron, magnesium, titanium, manganese, and aluminum, while x-ray diffraction has identified the presence of quartz (SiO<sub>2</sub>), gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), calcium-magnesium or calcium-aluminum silicates, and calcium phosphates (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH).

Further study provides the answer to the question of whether or not the typical brown coloring of the covering layers (visible in the cross sections of no. 2 in Fig. 7, no. 4 in Fig. 9 and no. 10 in Fig. 15) was pigmented.<sup>30</sup> Laser microanalysis demonstrates that practically no elements other than calcium and magnesium are to be found in the brown covering layers of Han era objects. For the moment the question must remain open as to whether the top layer was altered due to aging of the binding agent or was intentionally modified.

Finally, we come to the lacquer painting of a golden bird on a black ground from the Tang dynasty (no.11; Figs. 16,17,18; Mänchen-Helfen 1937a). This painting demonstrates several peculiarities in its pattern of elements and its cross section. It was not possible to explain the presence of gold in the dark layers of the black ground that appeared unpigmented under the microscope. The actual ornamental layer (Fig. 18) contains orpiment. The particles of metal visible in Figure 18 are tin, whereas silver foil could be detected in box no. 12 (Tang dynasty).

***Chinese carved  
lacquerware from  
Yuan to Qing***

Although taking samples from carved lacquerware is substantially more difficult, it was possible to examine a number of pieces, one from the Yuan dynasty (1279–1368; no. 14; Figs. 19–21), ten from the Ming dynasty (nos. 15–25; Figs. 22–39) and three from the Qing era (nos. 26–28; Figs. 40–42). In the case of nos. 16 and 18 sampling was restricted to the stand ring. Here, because of the ever-present possibility of overpainting, information on pigmentation could only be assessed with reservation.

While I am aware of the dangers of schematization, it appears feasible in the case of the objects examined here (mainly from the Ming dynasty), which had a number of features in common. The construction of these pieces can be described by a simple system of three functional zones: the base, a two-part ground, and an ornamental zone above that. On top of the base there is usually a thick layer of coarse, black ground. On top of that, there are three or four layers of a much harder and finer ground which is often yellow, or in any event a color different from that of the ornamental zone. Over this lie numerous lacquer bands, often with different pigmentations, which form a comparatively inelastic ornamental zone (Figs. 20,23, 26,29,31,32,34,39).

One might expect conservation and restoration problems similar to those found in panel painting and polychrome sculpture due to the conflicting properties of the mobile base and the immobile lacquer layers above. However, carved lacquerware is far less sensitive to variations in temperature and humidity than one would think (see section 5).



Figure 4. No. 1, wooden pedestal, China, end of Zhou dynasty (fifth–third century B.C.), Linden-Museum, Stuttgart (OA 20.739LA).

Figure 5. Cross section of no. 1 (Fig. 4; x160).

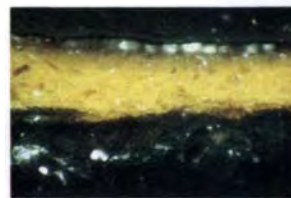


Figure 6. No. 2, two-eared cup, China, Zhan Guo era (fourth–third century B.C.; LMS OA 20.731L).

Figure 7. Cross section of no. 2 (Fig. 6; x32). The two laser craters are clearly visible here, as in the following photographs. The position of the craters permits the pattern of elements to be matched to its layer.

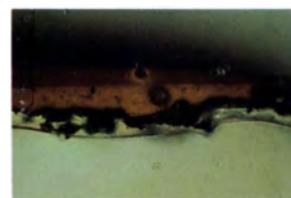


Figure 8. No. 4, round lidded box, China, late Zhou, beginning of Western Han dynasty, (c. second half of third century B.C.; LMS 20.720.L).

Figure 9. Cross section of No. 4 (Fig. 8; x32).

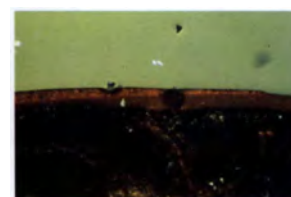


Figure 10. No. 8, two-eared cup, China, Eastern Han dynasty (100 B.C.–A.D. 100; LMS OA 20.736L).

Figure 11. Cross section of no. 8 (Fig. 10; x160).

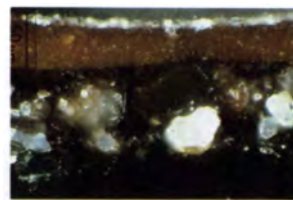


Figure 12. Cross section of No. 9 (not illustrated), two-eared cup, China, Han dynasty (100 B.C.– A.D. 100; LMS OA 20.735L; x80).

Figure 13. As for Figure 12, but in polarized light. The sequence of layers is clearly visible (x80).



Figure 14. No. 10, bowl, China, first half of the Eastern Han dynasty (first century; LMS OA 20.730L).

Figure 15. Cross section of No. 10 (Fig. 14; x63).

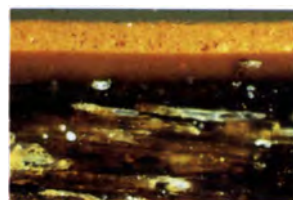


Figure 16. No. 11, lacquer painting, China, Tang dynasty (possibly later; LMS OA 20.848 a–gL).



Figure 17. Cross section of No. 11 (Fig. 16) in partly polarized light (x16).



Figure 18. Part of the cross section of no. 11 (Fig. 17), showing the uppermost layers (x200).



Figure 19. No. 14, bowl on stand, China, Yuan dynasty, probably fourteenth century (LMS OA 20.825a–bL).



Figure 20. Cross section of No. 14 (Fig. 19; x16).



Figure 21. Part of the cross section of no. 14 (Fig. 20) showing the lowest layers (x32).



Figure 22. No. 15, plate, China, Ming dynasty (late fourteenth–early fifteenth century; LMS OA 20.824L).



Figure 23. Cross section of No. 15 (Fig. 22; x32).



Figure 24. Part of the cross section of No. 15 (Fig. 23), showing the yellow ground layers (x63).



Figure 25. No. 19, large chest, China, Ming dynasty, Jiajing era (1522–1566) (LMS OA 20.761L).

Figure 26. Cross section of no. 19 (Fig. 25), upper layers (x16).  
Figure 27. Cross section of no. 19 (Fig. 25), lower layers (x40).

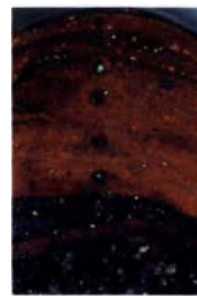


Figure 28. No. 21, plate, China, Ming dynasty, Wanli era, dated 1592 (LMA OA 20.756L).

Figure 29. Cross section of no. 21 (Fig. 28; x32).

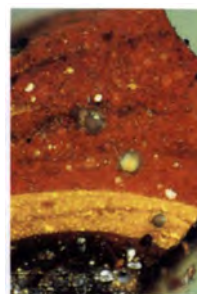


Figure 30. No. 22, box, China, Ming dynasty (second half of sixteenth century; LMS OA 20.763L).

Figure 31. Cross section of no. 22 (Fig. 30; x16). The position of the laser crater has been made visible with a white substance.

Figure 32. Part of the cross section of no. 22 (Fig. 31), showing the yellow ground layers and above them the black guide line (Garner 1963; x63).

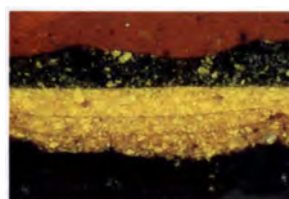


Figure 33. No. 23, box, China, Ming dynasty, Wanli era (1573–1619; LMS OA 20.819L).  
 Figure 34. Cross section of no. 23 (Fig. 33; x32).



Figure 35. No. 24, box, China, probably seventeenth century (LMS OA 20.765L).  
 Figure 36. Cross section of no. 24 (Fig. 35; x16).  
 Figure 37. Cross section of no. 24 (Fig. 35) in polarized light. The individual layers are clearly recognizable (x16).



Figure 38. No. 25, box, China, probably from the end of the Ming dynasty (sixteenth–seventeenth century; LMS OA 20.817L).  
 Figure 39. Cross section of no. 25 (Fig. 38; x32).

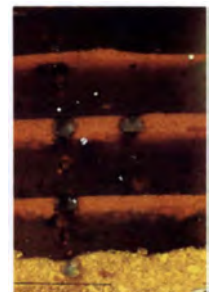


Figure 40. No. 28, box, China, Qing dynasty, dated 1775 (LMA OA 20.787L).

Figure 41. Cross section of no. 28 (Fig. 40; x16).

Figure 42. Part of cross section of no. 28 (Fig. 41); here the red layers were pigmented with vermilion (x63).



### **1. Bases and supports**

This study can say little about the nature of the base, that is, the type of wood used, even though x-rays appear to give very interesting results (Shosoin Office 1975). This is because cinnabar (the predominant pigment in the later objects) strongly absorbs x-rays (Rees-Jones 1975) and therefore the graining of the wooden base is very difficult to identify. Nonetheless, since x-ray investigations (unlike many older methods) do not damage the objects, they should not be forgotten, and an x-ray survey of the pieces is planned. The same reservation applies to the fabric often laid on top of the base (see Fig. 21, just visible at the bottom of the picture), which on intact pieces cannot be visually examined and sampled.

### **2. Black ground: construction, function, and pigmentation**

The lowest black ground contains mineral additives. High intensities of silicon, calcium, manganese, aluminum, titanium, iron, and magnesium indicate the use of dark earths, ashes, or clays.<sup>32</sup> According to experimental results, their proportion must be very high. The thickness of this layer is very striking and is often mentioned by Garner in his correspondence. This must have extended the drying time,<sup>33</sup> as well as prevented the formation of an urushi matrix without defects. However, it also leveled out any unevenness in the base below. Microscopic investigation does not reveal how many layers of this black ground were applied.

### **3. Yellow ground: construction and function**

In the series of pieces investigated from the Yuan and Ming dynasties, a further zone of ground is found above the thick black one. This zone consists of several layers; it is usually yellow (nos. 14,15,21,22,23,25 and Figs. 20,21,23,24,29,32, 34,39) or occasionally another color that in any case contrasts with the ornamental bands on top (brown-black in no. 19, Figs. 26,27, and black in no. 24, Figs. 36,37).

In contrast to the zone underneath, the proportion of binding agent is much higher in comparison to that of pigment and other material discussed later. This should result in increased stability. From a visual appraisal, it seems as though the surfaces of the layers have been very carefully worked (Figs. 21,24,32). This cannot be observed to such a great extent in the black zone beneath, and anyway is difficult to see because of the greater coarseness.

The first function of the yellow ground is to provide an additional leveling out of any unevenness in the black, coarse ground. Without this zone the layers above would follow any unevenness, which would greatly disturb the aesthetic

impression, especially in carved lacquerware with a different pigmentation of the ornamental zone.

Secondly, these layers absorb mechanical shearing forces between the wooden base and the ornamental zone. (The black zone below actually fulfils this function to an even greater extent.) The fact that these shearing forces often occur is mentioned in manuscripts from the fourteenth and fifteenth centuries which tell of the damage typical of carved lacquerware.<sup>34</sup>

The third function lies in conveying an optical impression of depth and at the same time in emphasizing the contours of the ornamentation because, in general, the yellow ground is exposed during carving in works of the Ming era, giving the impression that the ornamentation is painted on. The absence of this effect of depth on Qing dynasty piece no. 28 (Fig. 40) may account for its flatness and lifelessness, qualities also observed in pieces from the Ming era which are in need of cleaning.

A fourth and final function of the contrasting coloration of this zone was to aid the craftsman by giving him an indication of the maximum permitted cutting depth. After application and drying of the various layers, carving had to be done with extraordinary precision, as corrections were hardly possible. Therefore, it was of great importance that the depth of carving was uniform; the increased number of yellow layers permitted a certain, if limited, tolerance. The rubbing down of the surface of the black and yellow layers, already referred to, helped to maintain a uniform cutting depth.

#### ***4. Yellow ground: pigmentation***

There is evidence of arsenic<sup>35</sup> as a color-producing pigment in the yellow layers: diffractometric results on nos. 14,15,18, and 21 all clearly prove the use of orpiment (As<sub>2</sub>S<sub>3</sub>). The presence of calcium, magnesium, silicon, iron, mercury, aluminum, and manganese (listed here in order of their frequency, and most conspicuous in no. 21) point to a natural origin (Wallert 1984; Schafer 1955), whereby all these elements can be correlated to associated minerals (Schröcke 1981; Doelter 1926). Therefore it seems unlikely that synthetic orpiment (Wallert 1984; Schafer 1955) was used on the objects cited above. The presence of mercury can be explained by the natural admixture of cinnabar (Wallert 1984).<sup>36</sup> The earliest evidence of orpiment, within the limits of this investigation, can be traced to piece no.11 from the Tang era. In the case of carved lacquerware the evidence starts with no. 14 from the Yuan era and continues through to the Qing dynasty.

The literature shows that orpiment was used in Chinese painting from the ninth–tenth centuries A.D. (Winter 1984). Before that, yellow ocher and natural organic yellow pigments in China (Winter 1984; Gettens 1938–39) and also in Japan (Goffer 1980:177-179; Yamasaki 1979; FitzHugh 1979; Gettens 1976:241–252) were dominant from the beginning of the first century A.D. In Japan, orpiment was used frequently after the middle of the seventeenth century. Yonezawa (1956) gives some references to historical sources from the Six Dynasties onwards and refers to inland deposits in Southern China;<sup>37</sup> in fact the same regions in which there are large urushi plantations today. These key dates may, in association with the results of the present investigations, help to date and perhaps even to identify imitations.

#### ***5. The ornamental zone: construction and function***

The ornamental zone shows a huge range of styles as can be seen in Figures 20,23,26,31,36,39,41. Because of the slightly inhomogeneous distribution of pigments in the binding agent, the microscope reveals the differentiation between individual layers of lacquer, also clearly visible in the illustrations.

The condition of the surface of the layers in the cross sections sometimes suggests that very thorough treatment took place after the drying process. Exceptions are corners, edges, and heavily rounded sections, where working would be naturally more difficult and less regular. It is rare to encounter remains of abrasive materials such as in no. 14 (Fig. 21) which appear to have become embedded in layers which were not quite dry.

There is a great diversity in the literature on Chinese carved lacquerware about the number of layers involved. Estimates—and this is what is being discussed here—vary between a few and over 300 (Burmester and Brandt 1982). Garner attempts greater precision when he writes “the thickness of individual layers is in the order of 0.3 mm or less” and “between one and two hundred layers” (Garner 1979). Microscopic investigation of the pieces examined here permits a much more exact idea. If all the lacquer bands are included in the calculation, this gives an average thickness per layer of approximately 4 $\mu$ m.

Because of the many and various techniques which are dealt with in standard works on the subject, the question of further functions of the ornamental zone is not discussed here; it is obvious that this zone is open to visual examination (Garner 1979; Lee 1972; Kuwayama 1982).

The well thought out construction described above prevents variations in the moisture content of the base. Gain or loss of moisture is made extremely difficult due to the homogeneous, polymeric, and hydrophobic character of the lacquer layers. This explains the surprisingly good condition of some Chinese carved lacquerware. If a piece sustains mechanical damage, however, moisture can enter or leave, rapidly causing extensive damage because of the movement<sup>38</sup> of the base against the immobil ornamental zone.

#### *6. The ornamental zone: pigmentation of the red layers*

In the pieces examined—the early lacquerware<sup>39</sup> and the carved lacquerware<sup>40</sup>—mercury is found in the red pigmented layer almost without exception. This, together with the results of x-ray diffraction of samples from objects nos. 2,4–6,8, 9,12,13,15,16,18–26, and 28, proves that cinnabar (cinnabarite, beta-HgS) was used as a pigment.

Apart from mercury, other elements present (in order of frequency of occurrence) are calcium, magnesium, iron, silicon, manganese, arsenic, aluminum, barium, titanium, copper, chromium, and lead. These can be correlated to minerals associated with cinnabar (Schröcke 1981; Doelter 1926). The detection of this type of natural admixture using diffractometry proved to be possible on a few objects. However, an unambiguous matching was not achieved because it was not possible—for experimental reasons—to isolate only the red layers, that is, those which had been pigmented with cinnabar.

While it is possible to assume, from the impurities detected, that natural cinnabar was used in the majority of the pieces (nos. 15–23), this is not valid for the late Ming and Qing pieces (nos. 24–28). Apart from mercury, only calcium and magnesium could be detected, and these can be attributed to the binding agent itself. The absence of accompanying elements proves the application of vermilion, a synthetic cinnabar produced by repeated sublimation.<sup>41</sup> In relation to the dating of the pieces examined, this would indicate a change in the use of this important pigment from the seventeenth century onwards, and may be significant in providing further help in dating lacquerware. In pieces nos. 26 and 27 arsenic is also found, here certainly as orpiment. It is conceivable that in the purification of cinnabar by repeated sublimation, orpiment was carried through as an impurity. This is only possible for orpiment because it sublimes easily; it does not apply to other naturally associated minerals.



Data from the literature are very variable concerning the vermilion made from mercury and sulfur in the so-called dry process. Gettens (1972) says that the Chinese may have invented this process and that the earliest evidence for it is in the seventh century A.D. According to Needham (1976), the first written reference can be found as early as the fifth century B.C. From his comments, based on numerous sources, it is evident that cinnabar and mercury (often obtained from cinnabar) were the mainstays of Chinese alchemy and the related world of ideas. Therefore, it seems plausible that even before the seventh century, alchemists had made the observation that in the cooler areas of the experimental apparatus (ovens, furnaces, etc.) there were traces of a red substance—vermilion, resulting from sublimation. When this developed into a systematic process remains an open question.

Yamasaki (1979) reports vermilion being produced in Japan in 1609. According to Oguchi (1969), the synthetic pigment was widespread during the Edo period. These dates are compatible with the findings of the present investigation. Clear evidence of synthetic cinnabar in no. 17 supports the doubts expressed by art historians over dating the piece to the fifteenth century and identifying it as Chinese. It is more likely to be a later Japanese imitation of Chinese carved lacquerware.

In none of the cross sections was there a blackening of the red cinnabar when transformed into metacinnabar as discussed later on (Gettens 1972). Urushi appears to stabilize the pigment as well as an oily binding agent would do. The fact that this transformation can be observed is shown by the black coronae around the laser craters in Figures 23, 36, and 41. Black metacinnabar has formed here.

Compared with cinnabar, the other red pigments play a wholly subordinate role. Red iron oxide (haematite) was used as pigmentation in no. 14, in no. 19 in both upper layers, and in no. 26.<sup>42</sup> In nos. 14 and 26, the evidence could be secured by diffractometry. The choice of iron oxide was certainly due to its dull red tone, which differentiated it from the red of the surrounding layers derived from the presence of cinnabar. The pattern of elements in these dull red layers is especially pure. In particular, the pattern of no. 14 indicates very pure iron oxide, which was applied mixed with cinnabar in the other two cases.

The evidence of chromium in nos. 22 and 24 (Figs. 31,36, uppermost dark red layers) is puzzling; chromium pigments have only been known since the nineteenth century, so maybe this can be explained by restoration work.

### ***7. The ornamental zone: pigmentation of the black layers***

The pigmentation of the black layers of the lacquerware examined here requires more detailed consideration.

Once again, laser microanalysis offers clues as to the type of black pigments used. In the black layers there are remarkably frequent instances of iron,<sup>43</sup> mercury,<sup>44</sup> or spectra that are very low in elements and intensity.<sup>45</sup>

In the case of opaque pigmentation of the black layers (nos. 22 and 23), the evidence indicates that iron must be present as black iron pigments (as oxides or hydroxides), although it was not possible to support this by diffractometry.

For nos. 1, 8, 12, and 19 black metacinnabar could have been used in the opaque black layers. This is indicated by the presence of mercury, found by laser microanalysis, and proved additionally by x-ray diffractometry of nos. 1 and 19.<sup>46</sup> This result is very interesting because, as far as I know, metacinnabar has only been found once and confirmed by diffractometric analysis in a grave from the Han dynasty (Winter 1984).

It is obvious from the genesis of cinnabar and metacinnabar, as well as from the description of their deposits, that they are found associated as natural minerals. Furthermore, to the naked eye they are almost impossible to tell apart. If cinnabar is present as large crystals or crystal aggregates, then it is dark red, almost black. Only

after grinding will it become "cinnabar red." However, this means that a proportion of the minerals found in the natural deposits, that is, metacinnabar, remains black on grinding. Metacinnabar becomes red on heating, and mercury can also be obtained this way, so metacinnabar certainly had the same importance in alchemy as cinnabar or mercury. For these reasons, metacinnabar would have been an obvious choice as a black pigment; this is confirmed by the present findings.

However, in the remaining three pieces, nos. 14, 24, and 25, the black layers are transparent and, in addition to a similar brown-black coloration, only rarely contain small aggregates of black pigment (for example, no. 14, Figs. 20,21). The piece pictured in Figure 2 from Garner's estate shows a layer of similar appearance which, from its function, is referred to as a black guideline (Garner 1963, 1979; Burmester and Brandt 1982; see also Fig. 32). Garner's cross section in transmitted light shows the transparent character particularly clearly. In all these cases, the addition of carbon black can be assumed; this would explain the weak concentration of elements detected by laser microanalysis. Garner had already guessed as much and it can also be seen in many other objects of Far Eastern art (Winter 1984). Along with the use of soot or lamp black (Gettens 1938–39), the admixture of Chinese ink should also be considered. Thus Chiang-Yen (Yonezawa 1956) refers to Chinese ink as a dye as early as the fifth century, and Winter (1974) introduces other sources. Gettens (1976) and Yamasaki (1979) both name Chinese ink as the only black pigment in Japanese paintings. It is very interesting that Chinese ink (or more appropriately the glue used in its preparation) and urushi have a very similar pH (4–5; Reinhammar 1970). This has a positive effect on the compatibility of the ink with urushi. Because the hydrophobic character of soot would make it unsuitable as the only additive, it is better to mix it into hydrophilic glue which then stabilizes the colloidal system (Winter 1974). In connection with this there is an interesting reference in a source manuscript of Shen Chi-sun who reports the production of Chinese ink by combustion of urushi lacquer (Vaultier 1957).

***Pigments used in Chinese lacquerware and their relationship to Chinese philosophy***

A summary of all the pigments used in Chinese lacquerware investigated here gives for yellow, orpiment ( $\text{As}_2\text{S}_3$ ) and for red tones, cinnabar (beta-HgS) and occasionally haematite ( $\text{Fe}_2\text{O}_3$ ). For black hues there are metacinnabar (alpha-HgS), black iron pigments and carbon black as Chinese ink. Silver and tin have been detected as metal inlays. It is remarkable that none of the known blue and green pigments has been used.

In Winter's summary (1984), reference is made to the frequent application of other pigments in Chinese objects with other binding agent systems: for white, chalk ( $\text{CaCO}_3$ ) and "lead white" ( $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  and  $\text{PbSO}_4$ ), for blue, azurite ( $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ) and for green, malachite ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ) and copper chloride ( $\text{Cu}_2(\text{OH})_3\text{Cl}$  paratacamite and atacamite), though the presence of  $\text{PbSO}_4$  and  $\text{Cu}_2(\text{OH})_3\text{Cl}$  was exceptional.

Why are all these very common pigments not found in Chinese lacquerware? A few experiments, as well as reports from craftsmen, have demonstrated that chalk, lead white, azurite and malachite decompose in the binding agent urushi, that is they are unstable. The reason lies in the more acidic pH value of urushi: approximately 4.6 (Kenjo 1976) and 4.2 to 5.3 (Oshima 1985). This more acidic medium causes a chemical reaction which decomposes the pigment and gives a more basic pH value. This in turn deactivates the enzyme laccase (Reinhammar 1970), disturbs the equilibrium in the phenol-water emulsion and therefore hinders the drying of the urushi film (Kenjo 1976). The incompatibility of urushi with a large range of common pigments results in an inevitable limitation of colors used in Chinese lacquerwork.

I have already mentioned that cinnabar has a function as a reagent (Needham 1976) as well as a provider of color. It occupied a central role in the alchemy of ancient China, in daily life as well as in the Chinese spiritual world. Schafer (1955) assigns a similar role to orpiment. Because both cinnabar and orpiment can be repeatedly sublimed, they are bound closely to the concept of material immortality (Needham 1976). Objects made with urushi were regarded in the same way, as shown both by the great value placed upon them by the highest levels of society—including the imperial court—and by the fact that their production was, for a time, under state control (Garner 1979). Furthermore, lacquerware objects found in graves from the Han dynasty lasted until the Ming era and longer. This must have invested urushi with the mystical qualities of material immortality. The “mystery” surrounding urushi still disrupts the debate between east and west in matters of conservation and restoration. This combination of circumstances certainly did not go unnoticed and accounts for the unchanging high regard for urushi, cinnabar, and orpiment over a very long period.

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### **Appendix**

In the following section the results of microscopy and laser microanalysis are combined. For details of the methods of sampling see an earlier publication (Burmester and Brandt 1982). The cross sections, most of which are shown in Figures 4–42, were systematized in the following way. Each cross section contains lacquer bands (see note 29) A,B,C ... (first column), which are on either a wooden or a fabric base (T). Each band can incorporate *n* lacquer layers (see note 29) and is then referred to as *nx* (for example, 3D in the event that band D has three layers). In the second column a crude color is mentioned, in the third the function of the band and in the fourth its approximate thickness in  $\mu\text{m}$  (if not measurable, marked as \*). The last column gives the pattern of elements provided by laser microanalysis; the subscript numbers indicate the estimated intensity of the spectral lines from “only recognizable with difficulty” to “stronger than normal” and “auto reversal.” In cases where the laser beam did not penetrate exactly into a band, comments as to the positioning are given (for example, 80%A, 20%B, if 80% of the laser crater lies in band A). For technical reasons, memory effects could not be excluded in all cases.

Chinese lacquerware

1.	Wooden pedestal, China, end of Zhou (fifth-third century B.C.; Linden-Museum, Stuttgart, West Germany, OA 20.739A)			
A	black	ground	*	Si <sub>5</sub> , Fe <sub>5</sub> , Mg <sub>4</sub> , Al <sub>4</sub> , Ca <sub>4</sub> , Ti <sub>4</sub> , Hg <sub>4</sub> , Mn <sub>2</sub>
B	sand color			Ca <sub>3</sub> , Fe <sub>2</sub> , Cu <sub>2</sub> , Hg <sub>1</sub> , Mg <sub>1</sub> , Si <sub>1</sub>
C	black		<12	
2.	Two-eared cup, China, Zhan Guo era (fourth-third century B.C.; Linden-Museum, Stuttgart OA 20.731L; Brandt 1982, 1986).			
A	black	ground	*	Ca <sub>3</sub> , Si <sub>2</sub> , Ti <sub>2</sub> , Mg <sub>1</sub> , Fe <sub>1</sub>
B	sand	ground?	*	Ca <sub>3</sub> , Mg <sub>1</sub> , Si <sub>1</sub> , Fe <sub>1</sub>
C	brown		60	Ca <sub>3</sub> , Mg <sub>1</sub>
D	brown		<10	
3.	Lid of a vessel, China, end of Zhou (fourth-third century B.C.; Linden-Museum, Stuttgart OA 20.738L; Brandt 1986)			
A	black	ground	*	Ca <sub>2</sub> , Fe <sub>2</sub> , Cu <sub>2</sub> , Mg <sub>1</sub>
B	brown			Ca <sub>3</sub> , Fe <sub>3</sub> , Mg <sub>2</sub> , Si <sub>2</sub> , Cu <sub>2</sub> , Hg <sub>1</sub>
C	sand			Ca <sub>3</sub> , Mg <sub>2</sub> , Fe <sub>2</sub> , Si <sub>1</sub> , Cu <sub>1</sub>
4.	Round lidded box, China, late Zhou/beginning of Western Han (c. second half of third century B.C.; Linden-Museum, Stuttgart OA 20.720L; Brandt 1982, 1986)			
T				
A	brown-black	ground	*	Ca <sub>3</sub> , Al <sub>2</sub> , Mg <sub>1</sub> , Fe <sub>1</sub> , Hg <sub>1</sub>
B	brown		>50	90%B, 10%C: Ca <sub>3</sub> , Hg <sub>3</sub> , Mg <sub>1</sub>
C	red	ornament	15	Hg <sub>1</sub>
5.	Lid of a wine beaker of the "lian" type, China, probably Qin (227-206 B.C.; Linden-Museum, Stuttgart OA 20.719L)			
T				
A	sand	ground	75	10%A, 90%B: Ca <sub>4</sub> , Mg <sub>2</sub> , Si <sub>2</sub> , Fe <sub>2</sub> , Al <sub>1</sub>
B	brown		17	Ca <sub>4</sub> , Mg <sub>2</sub> , Si <sub>2</sub> , Fe <sub>2</sub> , Al <sub>1</sub>
6.	Internal construction of a box, China, Han dynasty, probably second half of second century B.C. (Linden-Museum, Stuttgart OA 20.721C)			
C	black	ornament	17	20%C, 70%B, 10%A: Ca <sub>3</sub> , Hg <sub>3</sub> , Si <sub>1</sub>
B	red		25	
A	brown-black	ground	*	
T	wooden core			
A'	black	ground	*	Ca <sub>5</sub>
B'	red	ornament	*	Ba <sub>4</sub> , Ca <sub>3</sub> , Cr <sub>3</sub> , Hg <sub>3</sub>
7.	Cylinder-shaped container, China, probably Western Han (200-100 B.C.; Linden-Museum, Stuttgart OA 20.722L)			
T				
A	brown	ground	*	
2B	brown		36	Ca <sub>3</sub> , Fe <sub>3</sub> , Mg <sub>1</sub> , Hg <sub>1</sub>
C	brown		30	
D	red		16	
8.	Two-eared cup, China, Eastern Han (100 B.C. - A.D. 100; Linden-Museum, Stuttgart OA 20.736L)			
A	black	ground	*	80%A, 20%B: Hg <sub>4</sub> , Si <sub>3</sub> , Ca <sub>3</sub> , Mn <sub>3</sub> , Fe <sub>3</sub> , Ba <sub>3</sub> , Mg <sub>2</sub> , Al <sub>1</sub> , Ti <sub>1</sub> , Cu <sub>1</sub>
B	brown		30	
9.	Two-eared cup, China, Han dynasty (100 B.C. - A.D. 100; Linden-Museum, Stuttgart OA 20.735L)			
A	black	ground	*	
B	black		>20	60%B, 40%C: Ca <sub>4</sub> , Hg <sub>4</sub> , Fe <sub>3</sub> , Mg <sub>2</sub> , Si <sub>1</sub> , Mn <sub>1</sub>
C	red		46	Ca <sub>4</sub> , Hg <sub>4</sub> , Fe <sub>3</sub> , Mg <sub>2</sub> , Mn <sub>2</sub>
D	black		6	
10.	Bowl, China, first half Eastern Han era (first century; Linden-Museum, Stuttgart OA 20.730L; Brandt 1986)			
T	wooden core			
A	black	ground	*	
B	brown		50	20%C, 80%B: Ca <sub>4</sub> , Mg <sub>3</sub> , Mn <sub>3</sub> , Fe <sub>3</sub> , Ba <sub>3</sub> , Hg <sub>3</sub> , Si <sub>1</sub>
C	red	ornament	55	Ca <sub>4</sub> , Ba <sub>3</sub> , Hg <sub>3</sub> , Fe <sub>2</sub> , Mg <sub>1</sub> , Si <sub>1</sub> , Mn <sub>1</sub>

<b>11. Seven lacquer paintings with gold-colored bird on a dark background, China, Tang dynasty, possibly later (Linden-Museum, Stuttgart OA 20.848a-gL; Brandt 1986)</b>				
from the surface of the painting:				
A	black	ground	*	Si <sub>4</sub> , Ca <sub>4</sub> , Fe <sub>4</sub> , Mg <sub>3</sub> , Ti <sub>3</sub> , Mn <sub>3</sub> , Al <sub>2</sub>
B	clear lacquer		70	Ca <sub>4</sub> , Sn <sub>3</sub> , Mg <sub>1</sub>
C	clear lacquer		50	
from the painting:				
A	brown-black	ground	*	Si <sub>4</sub> , Ca <sub>4</sub> , Fe <sub>4</sub> , Mg <sub>3</sub> , Ti <sub>3</sub> , Al <sub>2</sub> , Mn <sub>2</sub>
4B	brown		170	Au <sub>2</sub> , Ca <sub>1</sub>
C	sand	ornament	90	Sn <sub>5</sub> , Ca <sub>4</sub> , As <sub>3</sub> , Mg <sub>1</sub> , Si <sub>1</sub> , Fe <sub>1</sub>
		metal part		Sn <sub>7</sub> , Ca <sub>3</sub> , As <sub>3</sub> , Mg <sub>1</sub> , Al <sub>1</sub> , Si <sub>1</sub> , Fe <sub>1</sub>
D	clear lacquer		25	
E	clear lacquer		15	
<b>12. Heavily damaged lid or lower part of a box, China, Tang, c. eighth century (Linden-Museum, Stuttgart OA 20.744L; Brandt 1986)</b>				
T		wooden core		
(2?)A	black	ground	440	Ca <sub>5</sub> , Si <sub>4</sub> , Fe <sub>4</sub> , Mg <sub>2</sub> , Al <sub>2</sub> , Ag <sub>2</sub> , Hg <sub>1</sub>
B	brown	base	60	Ca <sub>4</sub> , Ag <sub>2</sub> , Hg <sub>2</sub>
C	red	ornament	50	Ca <sub>4</sub> , Ag <sub>4</sub> , Hg <sub>2</sub>
<b>13. Small petal-edged bowl with flat bottom, China, Song dynasty, c. twelfth-thirteenth century (Linden-Museum, Stuttgart OA 20.746L)</b>				
T				
A	black	ground	*	
B	clear lacquer	25		Ca <sub>8</sub> , Mg <sub>4</sub> , P <sub>4</sub> , Mn <sub>3</sub> , Fe <sub>3</sub> , Al <sub>1</sub> , Si <sub>1</sub>
C	red	ornament	30	
<b>Chinese carved lacquerware</b>				
<b>14. Bowl on a stand, China, Yuan dynasty, probably fourteenth century (Linden-Museum, Stuttgart OA 20.825a+bL; Brandt 1982, 1986)</b>				
T				
A	black	ground	*	Ca <sub>4</sub>
4B	yellow	yellow ground	200	Ca <sub>4</sub> , As <sub>3</sub> , Mg <sub>2</sub>
7C	black		230	Ca <sub>4</sub> , Mg <sub>2</sub>
3D	red		150	Ca <sub>4</sub> , Fe <sub>4</sub> , Mg <sub>2</sub>
4E	black		260	Ca <sub>4</sub> , Mg <sub>2</sub>
2F	red		200	Ca <sub>4</sub> , Fe <sub>4</sub> , Mg <sub>2</sub>
6G	black		250	Ca <sub>1</sub>
<b>15. Plate, China, Ming dynasty, late fourteenth-early fifteenth century (Linden-Museum, Stuttgart OA 20.824L)</b>				
T				
A	black	ground	*	Si <sub>4</sub> , Ca <sub>4</sub> , Mn <sub>4</sub> , Al <sub>3</sub> , Ti <sub>3</sub> , Fe <sub>3</sub> , Mg <sub>1</sub>
B	yellow	yellow ground	*	
4C	yellow	yellow ground	360	As <sub>3</sub> , Hg <sub>3</sub> , Ca <sub>2</sub>
7D	red		} 390	90%D, 10%E: Hg <sub>5</sub> , Fe <sub>3</sub> , Ca <sub>3</sub> , Mg <sub>1</sub> , Al <sub>1</sub> , Si <sub>1</sub> , As <sub>1</sub>
E	black			
7F	red		} 290	
G	black			
7H	red		} 170	Hg <sub>5</sub> , Ca <sub>3</sub> , Fe <sub>2</sub> , Mg <sub>1</sub> , Al <sub>1</sub> , Si <sub>1</sub>
I	black			
7J	red		} 230	
K	black			
7L	red		} 210	
M	black			
10N	red		380	
<b>16. Box, China, Ming dynasty, Yongle era (1403–1424; Linden-Museum, Stuttgart OA 20.753L; Brandt 1982, 1986)</b>				
	red layer			Hg <sub>7</sub> , Ca <sub>5</sub> , Fe <sub>2</sub> , Mg <sub>1</sub> , Si <sub>1</sub>

<b>17.</b> Large plate, China, Ming dynasty, second half of fifteenth century (Linden-Museum, Stuttgart OA 20.754L); this could also be considerably later and of Japanese origin				
	black layer			Hg <sub>5</sub> , Ca <sub>3</sub> , Mg <sub>1</sub> (contaminated with red layer by 30%)
	numerous red layers			Hg <sub>6</sub> , Ca <sub>3</sub> , Mg <sub>1</sub>
	aggregate of pigment in red layer			Hg <sub>6</sub> , Ca <sub>3</sub> , Mg <sub>1</sub>
<b>18.</b> Bowl, China, Ming dynasty, Jiajing era (1522–1566; Linden-Museum, Stuttgart OA 20.796L)				
A	black	ground	*	
B	yellow-brown		<160	
C	black		650	Hg <sub>5</sub> , Ca <sub>4</sub> , Mg <sub>3</sub> , Mn <sub>3</sub> , Si <sub>1</sub> , Fe <sub>1</sub>
D	red		110	Hg <sub>5</sub> , Ca <sub>4</sub> , Mn <sub>4</sub> , Mg <sub>3</sub> , Cu <sub>2</sub> , Si <sub>1</sub> , Fe <sub>1</sub>
<b>19.</b> Large chest, China, Ming dynasty, Jiajing era (1522–1566; Linden-Museum, Stuttgart OA 20.761L; Brandt 1986)				
A	black	ground	*	Ca <sub>4</sub> , Hg <sub>3</sub>
B	black	ground	*	
C	brown		80	Ca <sub>4</sub> , Fe <sub>4</sub> , Hg <sub>4</sub> , Mn <sub>3</sub> , Mg <sub>2</sub> , Si <sub>1</sub> , As <sub>1</sub>
D	black		240	Ca <sub>4</sub> , Hg <sub>4</sub> , As <sub>3</sub> , Mn <sub>3</sub> , Mg <sub>1</sub> , Si <sub>1</sub> , Fe <sub>1</sub>
13E	red		1040	Hg <sub>6</sub> , Ca <sub>4</sub> , Mg <sub>2</sub> , Mn <sub>2</sub> , Fe <sub>1</sub> , As <sub>1</sub> Hg <sub>6</sub> , Ca <sub>3</sub> , Mg <sub>2</sub> , Mn <sub>2</sub> , Si <sub>1</sub> , Fe <sub>1</sub> , As <sub>1</sub> Hg <sub>5</sub> , Ba <sub>4</sub> , Ca <sub>3</sub> , Mg <sub>1</sub> , Mn <sub>1</sub> , Fe <sub>1</sub>
5F	brown		320	Fe <sub>6</sub> , Hg <sub>3</sub> , Al <sub>3</sub> , Si <sub>3</sub> , Ca <sub>3</sub> , Mn <sub>3</sub> , Ti <sub>2</sub> , Mg <sub>1</sub>
2G	dark red		60	Fe <sub>6</sub> , Hg <sub>4</sub> , Si <sub>4</sub> , Ca <sub>4</sub> , Al <sub>3</sub> , Mn <sub>3</sub> , Ti <sub>2</sub> , Mg <sub>1</sub>
<b>20.</b> Large round box with multicolored carved lacquer, China, Ming dynasty, Wanli era, dated 1586 (Linden-Museum, Stuttgart OA 20.807L; Brandt, 1982, 1986)				
T				
A	black	ground	*	Si <sub>4</sub> , Ca <sub>4</sub> , Fe <sub>4</sub> , Mg <sub>3</sub> , Ti <sub>3</sub> , Mn <sub>3</sub> , Al <sub>2</sub> , Hg <sub>2</sub>
B	red		*	10%A, 90%B: Ca <sub>4</sub> , Hg <sub>4</sub> , Mg <sub>3</sub> , Si <sub>3</sub> , Mn <sub>3</sub> , Fe <sub>3</sub>
2C	red		120	Ca <sub>3</sub> , Hg <sub>3</sub> , Mg <sub>1</sub> , Si <sub>1</sub> , Fe <sub>1</sub>
D			10	
<b>21.</b> Large plate with seven dragon medallions, China, Ming dynasty, Wanli era, dated 1592 (Linden-Museum, Stuttgart OA 20.756L; Brandt, 1982, 1986)				
A	black	ground	*	Ca <sub>5</sub> , Mg <sub>4</sub> , Si <sub>4</sub> , Fe <sub>4</sub> , Ti <sub>3</sub> , Mn <sub>3</sub> , Hg <sub>3</sub> , Al <sub>2</sub> , As <sub>1</sub>
4B	yellow	yellow ground	140	Ca <sub>5</sub> , Mg <sub>4</sub> , Fe <sub>4</sub> , As <sub>4</sub> , Si <sub>3</sub> , Mn <sub>3</sub> , Hg <sub>3</sub> , Al <sub>1</sub>
7C	red		>430	Hg <sub>6</sub> , Ca <sub>5</sub> , Mg <sub>4</sub> , Si <sub>3</sub> , Fe <sub>3</sub> , Mn <sub>2</sub> , Al <sub>1</sub> , As <sub>1</sub> Hg <sub>6</sub> , Ca <sub>5</sub> , Mg <sub>4</sub> , Si <sub>4</sub> , As <sub>4</sub> , Fe <sub>3</sub> , Ti <sub>2</sub> , Mn <sub>2</sub> , Al <sub>1</sub> Ca <sub>5</sub> , Hg <sub>4</sub> , Mg <sub>2</sub> , Si <sub>1</sub> , Fe <sub>1</sub> , As <sub>1</sub> Ca <sub>5</sub> , Hg <sub>4</sub> , Mg <sub>2</sub> , Si <sub>1</sub> , Mn <sub>1</sub> , Fe <sub>1</sub> , As <sub>1</sub>
<b>22.</b> Octagonal box, China, Ming dynasty, second half of sixteenth century; Linden-Museum, Stuttgart OA 20.763L; Brandt 1986)				
A	black	ground	*	Si <sub>5</sub> , Ca <sub>4</sub> , Fe <sub>4</sub> , Mg <sub>3</sub> , Al <sub>3</sub> , Ti <sub>3</sub> , Mn <sub>2</sub> , Hg <sub>1</sub>
B	yellow	yellow ground	*	Ca <sub>5</sub> , As <sub>4</sub> , Mg <sub>2</sub> , Si <sub>1</sub> , Fe <sub>1</sub> , Hg <sub>1</sub>
2C	yellow	yellow ground	80	
D	black guide line	black	80	80%D, 20%E: Ca <sub>5</sub> , Fe <sub>5</sub> , Mg <sub>2</sub> , As <sub>2</sub> , Si <sub>1</sub> , Mn <sub>1</sub>
E	dark red		90	Ca <sub>5</sub> , Fe <sub>5</sub> , Hg <sub>3</sub> , Mg <sub>2</sub> , Mn <sub>2</sub> , Si <sub>1</sub> , As <sub>1</sub>
39F	red		1550	Hg <sub>5</sub> , Ca <sub>3</sub> , Ba <sub>3</sub> , Fe <sub>2</sub> , Mg <sub>1</sub> , As <sub>1</sub> Hg <sub>4</sub> , Ca <sub>3</sub> , Fe <sub>3</sub> , Ba <sub>3</sub> , Mg <sub>1</sub> , Cr <sub>1</sub> , Pb <sub>1</sub> Ba <sub>3</sub> , Ca <sub>2</sub> , Fe <sub>2</sub> , Hg <sub>2</sub>
<b>23.</b> Rectangular lidded box, China, Ming dynasty, Wanli era (1573–1619; Linden-Museum, Stuttgart OA 20.819L; Brandt 1986)				
A	black	ground	*	
B	yellow	yellow ground	*	
3C	yellow	yellow ground	190	As <sub>4</sub> , Ca <sub>2</sub> , Mg <sub>1</sub>
5D	black		250	Fe <sub>3</sub> , As <sub>2</sub> , Ca <sub>2</sub> , Hg <sub>2</sub> , Mg <sub>1</sub>
E	red		100	Hg <sub>5</sub> , Fe <sub>4</sub> , Ca <sub>3</sub> , As <sub>2</sub> , Mg <sub>1</sub> , Si <sub>1</sub>
6F	black		340	
3G	red		65	
8H	black		250	
2I	red		85	
4J	dark red		110	

<b>24. Rectangular box, China, probably seventeenth century (Linden-Museum, Stuttgart OA 20.765L)</b>				
2B'	black	interior	60	Ca <sub>3</sub> , Si <sub>1</sub>
A'	black	ground	>850	Ca <sub>8</sub> , Ti <sub>5</sub> , Mg <sub>4</sub> , Mn <sub>4</sub> , Fe <sub>4</sub> , Al <sub>3</sub> , Si <sub>3</sub>
T		wooden core		
A	black	ground	*	Si <sub>4</sub> , Ca <sub>4</sub> , Ti <sub>4</sub> , Fe <sub>4</sub> , Mg <sub>3</sub> , Al <sub>3</sub> , Mn <sub>3</sub>
B	black		50	
2C	black		180	50%B, 50%C: Si <sub>4</sub> , Ca <sub>4</sub> , Fe <sub>4</sub> , Mg <sub>3</sub> , Al <sub>3</sub> , Ti <sub>3</sub> , Mn <sub>2</sub>
9D	red-brown		425	Ca <sub>3</sub> , Hg <sub>3</sub>
2E	light red		85	Hg <sub>4</sub> , Ca <sub>3</sub> , Mg <sub>1</sub>
F	black		65	30%E, 70%F: Hg <sub>5</sub> , Ca <sub>3</sub> , Mg <sub>2</sub> , Si <sub>2</sub> , Fe <sub>2</sub> 20%E, 80%F: Hg <sub>5</sub> , Ca <sub>2</sub> , Si <sub>1</sub> , Fe <sub>1</sub>
G	light brown		65	
H	brown		20	70%G, 30%H: Ca <sub>2</sub> , Fe <sub>2</sub> , Hg <sub>2</sub> , Si <sub>1</sub>
11I	brown-red		620	Ca <sub>3</sub> , Hg <sub>3</sub> , Mg <sub>1</sub>
J	clear lacquer	exterior	30	30%I, 70%J: Fe <sub>5</sub> , Cr <sub>4</sub> , Hg <sub>4</sub> , Ca <sub>3</sub> , Ba <sub>3</sub> , Pb <sub>3</sub> , Mn <sub>2</sub>
<b>25. Rectangular box, probably China, probably end of Ming dynasty, sixteenth-seventeenth century (Linden-Museum, Stuttgart OA 20.817L)</b>				
A	black	ground	*	
B	yellow	yellow ground	*	
3C	yellow	yellow ground	150	As <sub>4</sub> , Ca <sub>2</sub> , Hg <sub>2</sub> , Mg <sub>1</sub> , Si <sub>1</sub> , Fe <sub>1</sub>
5D	black		} 210	Si <sub>2</sub> , Ca <sub>2</sub> , Hg <sub>2</sub> , Mg <sub>1</sub> , Fe <sub>1</sub> , As <sub>1</sub> Hg <sub>4</sub> , Ca <sub>2</sub>
E	red			
5F	black		} 290	Ca <sub>1</sub> , Hg <sub>1</sub> Hg <sub>4</sub> , Ca <sub>2</sub> , Mg <sub>1</sub> , As <sub>1</sub>
G	red			
5H	black		} 250	Hg <sub>3</sub> , Ca <sub>1</sub> , As <sub>1</sub>
I	red			
5J	black		} 235	Ca <sub>4</sub> , Hg <sub>3</sub>
K	red			
5L	black		} 290	
M	red			
7N	black		290	
<b>26. Large table with carved lacquerwork, late seventeenth-early eighteenth century (Linden-Museum, Stuttgart OA 20.748L); samples taken from the upper surface of the table, small particles without ground.</b>				
	numerous red layers alternating			red: Fe <sub>4</sub> , As <sub>3</sub> , Hg <sub>3</sub> , Ca <sub>2</sub> , Mg <sub>1</sub>
	with red brown layers			red-brown: Fe <sub>5</sub> , Ca <sub>2</sub> , Hg <sub>2</sub> , Mg <sub>1</sub> , Mn <sub>1</sub>
<b>27. Square vase in the form of a "ku," China, Qing dynasty, bearing the mark of the Quianlong era (1736–1795) (Linden-Museum, Stuttgart OA 20.055); sample taken from the ornament in the foot.</b>				
	numerous ground layers			Ca <sub>5</sub> , Mg <sub>3</sub> , As <sub>3</sub> , Si <sub>2</sub> , Mn <sub>1</sub> , Al <sub>1</sub> , Fe <sub>1</sub>
	numerous red layers			Hg <sub>6</sub> , As <sub>3</sub> , Ca <sub>2</sub> , Mg <sub>1</sub>
<b>28. Twelve-cornered box, China, Qing dynasty, dated 1775 (Linden-Museum, Stuttgart OA 20.787L)</b>				
A	black	ground	*	Ca <sub>4</sub>
>20B	black	yellow ground	>1150	Ca <sub>4</sub>
8C	red		495	Ca <sub>3</sub> , Hg <sub>3</sub>

1. In Garner's estate there is a series of handwritten technical notes dated 6.7.62, 26.7.62, 28.7.62, 1.8.62, 11.2.63, and 25.11.63.
2. The results were communicated to Garner by E.W.S. Press, Director of Chemical Inspection, War Office, London, dated 4.12.61 and 30.10.62.
3. Experiments by A.E. Werner, Research Laboratory, British Museum, London, dated 27.11.62.
4. For example, in a letter dated 27.11.63, the Swedish King Gustav Adolf VI suggested a further examination of a piece from his collection.
5. R.J. Gettens, Freer Gallery of Art, Washington, 7.5.63. A schematic drawing of the construction by E.W. FitzHugh was included.
6. A.R. Sollars, Department of Materials, College of Aeronautics, Cranfield, Bletchley, Buckinghamshire, 17.6.63. It is clear from the letter that Sollars must have examined several samples for Garner. It is possible that the discussion was about one of Garner's cross sections (1963) without it being referred to specifically. There is a photograph in that article (Fig. 4, "magnification about x8") which bears a reference to A.R. Sollars of Cranfield ("magnification x10").
7. For example, H. Trubner of the Royal Ontario Museum, University of Toronto, sent him a sample of a pre-Han or Lo-yang piece.
8. P.H. Plesch, University of Keele, 29.9.65.
9. On 2.3.64 from Inv. 53.8 of the Freer Gallery of Art, Washington, D.C.
10. On 13.1.66 by A.E. Werner, British Museum, London.
11. V.A. Moss requests an answer to this in his letter of 18.4.67.
12. In a letter to J. Needham on 28.12.66 and in correspondence with his nephew V.A. Moss on 15.10.69 and 20.10.72.
13. In letters to J.S. Mills, National Gallery, London (answered on 11.7.70) and V.A. Moss (answered on 6.5.71) and in debate with R.C.A. Rottländer of the Labor für Bernsteinforschung, Bonn, on suggested procedures using infrared spectroscopy and field ionization mass spectroscopy.
14. In response to a suggestion from his nephew V.A. Moss, Garner writes on 20.10.72: "I will alter 'urushic acid' to 'urushiol.' Should I not also alter 'acids' . . . . to 'components'?"
15. Thus on 11.12.69 Garner receives from Sir G. Taylor, Director of the Royal Botanical Gardens, Kew, Richmond, Surrey, the information that "*R(hus) vernicifera* DC is a synonym of *R(hus) verniciflua* Stokes; the latter is the correct name for this species."
16. In many letters and in an updated outline of the second chapter of his book (Garner 1979).
17. In a letter to R.J. Gettens of 8.5.68, Garner writes: "Among the known (Han) lacquer pieces, I would say that less than 5% have fabric." However, Gettens had informed him long before that (2.3.64) that he had found no fabric supports in the pieces studied from the Freer Gallery.
18. The cross section bears the note "15th C. strong black layer," which may refer to the heavily applied "black guide line" (Garner 1963). Unfortunately, the origin of the sample and the name of the preparer are unknown. An additional cross section of a "16th C." piece should also be mentioned here.
19. On 24.4.68 R.J. Gettens sends a "Summary of an examination made of Han lacquer fragments supplied by Sir Harry Garner . . ." written by W.T. Chase.
20. One reason for this may be that urushi is not used as a binding agent in the West, yet the analysis of binding agents has been developed largely in the West.
21. J.S. Mills to Garner, 11.7.70.
22. These results may rest on the observation that earlier lacquers differ radically from later ones, an observation that has never been satisfactorily explained (Burmester 1983b).
23. High-resolution mass spectrometry was carried out on the samples discussed here, nos. 1, 2, 4, 5, 7-9, 11, 12, 14-16, 18-24, 28 on two pieces of Chinese carved lacquerware dated 1586 (OA 20.813L) and second half, eighteenth century (OA 20.804bL), on a Japanese *sake* bowl of the second half of the nineteenth century (9.645B) and on three recent examples from Japan and Thailand. The three additional pieces were also from the collection of the Linden-Museum in Stuttgart. The high-resolution mass spectra of these samples usually showed high intensities for the following masses (in order of their calculated C,H,O compositions): C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>, C<sub>6</sub>H<sub>9</sub>, C<sub>7</sub>H<sub>5</sub>O, C<sub>4</sub>H<sub>9</sub>O<sub>3</sub>, C<sub>8</sub>H<sub>11</sub>, C<sub>7</sub>H<sub>7</sub>O, C<sub>7</sub>H<sub>8</sub>O, C<sub>8</sub>H<sub>13</sub>, C<sub>7</sub>H<sub>9</sub>O, C<sub>7</sub>H<sub>11</sub>O, C<sub>9</sub>H<sub>7</sub>, C<sub>9</sub>H<sub>9</sub>, C<sub>9</sub>H<sub>11</sub>, C<sub>8</sub>H<sub>9</sub>O, C<sub>7</sub>H<sub>7</sub>O<sub>2</sub>, C<sub>7</sub>H<sub>8</sub>O<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>O<sub>3</sub>, C<sub>10</sub>H<sub>9</sub>, C<sub>10</sub>H<sub>9</sub>, C<sub>9</sub>H<sub>7</sub>O, C<sub>8</sub>H<sub>11</sub>O, C<sub>6</sub>H<sub>8</sub>O<sub>2</sub>, C<sub>6</sub>H<sub>9</sub>O<sub>2</sub>, C<sub>10</sub>H<sub>9</sub>O, C<sub>8</sub>H<sub>9</sub>O<sub>2</sub>, C<sub>9</sub>H<sub>15</sub>O<sub>3</sub>.
24. Depending on their date, the pieces examined<sup>23</sup> demonstrated the following high-intensity peaks: C<sub>6</sub>H<sub>5</sub>O<sub>2</sub> for Yuan (Y) and Ming (M); C<sub>6</sub>H<sub>14</sub> for Zhou (Z) and Qing (Q); C<sub>7</sub>H<sub>10</sub>O for M and Q; C<sub>6</sub>H<sub>15</sub> for Z, Q and modern lacquers (mo); C<sub>7</sub>H<sub>12</sub>O M, Q; C<sub>6</sub>H<sub>8</sub>O<sub>2</sub> M, Q; C<sub>5</sub>H<sub>6</sub>O<sub>3</sub> Y, M, Q; C<sub>7</sub>H<sub>9</sub>O<sub>2</sub> late M, Q and mo; C<sub>6</sub>H<sub>13</sub>O Han (H) to mo; C<sub>6</sub>H<sub>8</sub>O<sub>3</sub> Y, M, and early Q; C<sub>6</sub>H<sub>10</sub>O<sub>3</sub> Q, mo; C<sub>6</sub>H<sub>9</sub>O Q, mo; C<sub>8</sub>H<sub>10</sub>O<sub>2</sub> late Y to mo; C<sub>10</sub>H<sub>18</sub> Z, H; C<sub>8</sub>H<sub>12</sub>O<sub>2</sub> Y to Q; C<sub>9</sub>H<sub>15</sub>O<sub>2</sub> Z to Q; C<sub>11</sub>H<sub>15</sub>O late M and Q; C<sub>12</sub>H<sub>19</sub> Z; C<sub>13</sub>H<sub>9</sub> Q and mo; C<sub>12</sub>H<sub>21</sub> Z; C<sub>12</sub>H<sub>13</sub>O Q and mo; C<sub>11</sub>H<sub>10</sub>O<sub>2</sub> M to mo; C<sub>10</sub>H<sub>9</sub>O<sub>3</sub> Z and mo; C<sub>12</sub>H<sub>10</sub>O<sub>2</sub> mo; C<sub>12</sub>H<sub>12</sub>O<sub>2</sub> mo; C<sub>15</sub>H<sub>28</sub> Z and C<sub>14</sub>H<sub>28</sub>O<sub>3</sub> mo. It should be made clear that this note and the previous one<sup>23</sup> are intended merely to convey experimental results, not to deliver broad conclusions.
25. The equipment and parameters used in the experiments conducted here were: Laser Microspectral Analyzer IMA 10 (Jenoptik Jena) with Quartz Spectrograph Q24, Q-switch-cuvette 2, diaphragm 1(2), magnification 40(16), lamp voltage 0.9kV, battery I, spark voltage 4kV, induction 125μH, delay time 400μsec., electrode gap 1.6 mm, electrode-to-sample gap 1.2 mm; Q24: width of slit 15μ, slit height 1 mm, aperture 1:15.
26. Zeiss photomicroscope II with dark field illuminator. Film: Kodak Ektachrome, artificial light, 160 ASA.
27. Philips PW 1700 automatic powder diffraction system, Cu-fine-focus tube 40kV/30mA.
28. The high proportion of amorphous binding agent urushi proved to be a problem here, in that it produced a very high background.
29. Lacquer bands, according to Garner's definition (1963) are made up of several lacquer layers which have the same pigmentation and therefore the same color.



30. An analytical review of the corresponding layers of no. 2 shows low intensities of Ca<sub>3</sub> and Mg<sub>1</sub> (for notation see Appendix); of no. 4, cinnabar (HgS, see below) contaminated from the ornamental layer<sup>31</sup>, Ca<sub>3</sub>, Hg<sub>3</sub>, and Mg<sub>1</sub>; and, contaminated in the same fashion, in no. 10, Ca<sub>4</sub>, Mg<sub>3</sub>, Fe<sub>3</sub>, Ba<sub>3</sub>, Hg<sub>3</sub> and Si<sub>1</sub>. As explained in detail below, all elements except manganese can be traced back to the application of natural cinnabar, originating (as in no. 4) in the ornamental zone.

31. In individual cases it was extremely difficult to direct the laser beam onto the selected lacquer layer because the microscope used for selection did not permit color observation.

32. Mänchen-Helfen (1937b) brings to our attention a section of the *Cho-keng lu* of Tao Tsung-yi (A.D. 1366 which is concerned with the ground:

"The lacquer workers buy the objects to be decorated from the turners. They are made of thin, soft pieces of wood bound by glue. First the joints are smoothed and any gaps filled with a mixture of natural lacquer and glue, called *shao-tang*. . . . They cover the object with a layer of lacquer. On top of this they place a linen cloth. The first layer of ash is then applied. In all, three layers of ash are used, mixtures of ash, powdered brick and lacquer and ever finer ash. Each layer, as soon as it is dry, is polished with sand leather [like our glass paper]. For cheaper products a mixture of pig's blood and rice paste is used and, instead of linen, hemp. On top of the last layer of ash, there is another layer of lacquer—*tsao ch'i*. . . and in this way the object has been well primed. When red lacquer is used, there is no *tsao ch'i*."

The question must be raised, both here and for other sources, as to whether the translation is accurate (e.g. linen and hemp). Garner spent years pondering this issue as can be seen by the bibliography of his book (1979).

33. The increased thickness of the layer naturally extends the drying period. In reference to this, Garner (1979) quotes from the *Cho-keng lu* of Tao Tsung-yi (A.D. 1366):

"... referring to the meticulous care with which the ground work was done and each layer polished before the next was applied. It mentions that several months elapsed between the preparation of the base and the application of the first coloured layer."

In comparison, the drying time for a lacquer layer in the ornamental zone is between four and five days.

34. Mänchen-Helfen (1937b) translates from the *Ko-ku-yao-lun* of Ts'ao Chao of A.D. 1388 (edited 1459):

"... the objects produced lately under Yüan in Yang-hui and Si-t'ang, Kia-hing-fu have many layers and are carved in strong relief, but the fat content of the lacquer is too low. There are many well-worked pieces but the lacquer flakes off very easily on those with yellow ground."

This is further evidence that the adhesion is weakened between the yellow ground and the ornamental zone. This concept is supported by a comment about a Chinese *guri* lacquer bowl (fifteenth-sixteenth century) by Gabbert (1978):

"the yellow lacquer layers sometimes seem to have the effect of raising the ornamented sections."

However, this raising of the ornamental sections was due not to the yellow layers but to the movement<sup>38</sup> of the wood with respect to the stability of the ornamental zone.

35. In no. 11 (Fig. 18) as (Sn<sub>5</sub>), Ca<sub>4</sub>, As<sub>3</sub>, Mg<sub>1</sub>, Si<sub>1</sub>, Fe<sub>1</sub> and (Sn<sub>7</sub>), Ca<sub>3</sub>, As<sub>3</sub>, Mg<sub>1</sub>, Al<sub>1</sub>, Si<sub>1</sub>, Fe<sub>1</sub>; no. 14 (Fig. 20, 21) as Ca<sub>4</sub>, As<sub>3</sub>, Mg<sub>2</sub>; no. 15 (Fig. 23, 24) as As<sub>3</sub>, Hg<sub>3</sub>, Ca<sub>2</sub>; no. 21 (Fig. 29) as Ca<sub>5</sub>, Mg<sub>4</sub>, Fe<sub>4</sub>, As<sub>4</sub>, Si<sub>3</sub>, Mn<sub>3</sub>, Hg<sub>3</sub>, Al<sub>1</sub>; no. 22 (Fig. 31, 32) as Ca<sub>5</sub>, As<sub>4</sub>, Mg<sub>2</sub>, Si<sub>1</sub>, Fe<sub>1</sub>, Hg<sub>1</sub>; no. 23 (Fig. 34) as As<sub>4</sub>, Ca<sub>2</sub>, Mg<sub>1</sub> and in no. 25 (Fig. 39) as As<sub>4</sub>, Ca<sub>2</sub>, Mg<sub>1</sub>, Si<sub>1</sub>, Fe<sub>1</sub>. Here and in notes 35, 38–40 and 42–45 only those results are given in which there was no possibility of contamination from other layers.

36. Garner (1963) explains evidence of mercury in the yellow ground as contamination from the ornamental zone above, but this interpretation can now be excluded.

37. However, it can be assumed that orpiment, like other pigments (especially cinnabar), was available from other Chinese provinces (Yonezawa 1956) and was imported from abroad.

38. Movement of wood refers to dimensional change arising from a variation in moisture content.

39. On no. 4 (Fig. 9): Hg<sub>1</sub> (low intensity spectrum); no. 6: Ba<sub>4</sub>, Ca<sub>3</sub>, Cr<sub>3</sub>, Hg<sub>3</sub>; no. 9 (Figs. 12, 13): Ca<sub>4</sub>, Hg<sub>4</sub>, Fe<sub>3</sub>, Mg<sub>2</sub>, Mn<sub>2</sub>; no. 10 (Fig. 15): Ca<sub>4</sub>, Ba<sub>3</sub>, Hg<sub>3</sub>, Fe<sub>2</sub>, Mg<sub>1</sub>, Si<sub>1</sub>, Mn<sub>1</sub>; no. 12: Ca<sub>4</sub>, Ag<sub>4</sub>, Hg<sub>2</sub>.

40. No. 15 (Fig. 23): Hg<sub>5</sub>, Ca<sub>3</sub>, Fe<sub>2</sub>, Mg<sub>1</sub>, Al<sub>1</sub>, Si<sub>1</sub>; no. 16: Hg<sub>7</sub>, Ca<sub>5</sub>, Fe<sub>2</sub>, Mg<sub>1</sub>, Si<sub>1</sub>; no. 17: twice Hg<sub>6</sub>, Ca<sub>3</sub>, Mg<sub>1</sub>; no. 18: Hg<sub>5</sub>, Ca<sub>4</sub>, Mg<sub>3</sub>, Mn<sub>3</sub>, Si<sub>1</sub>, Fe<sub>1</sub> and Hg<sub>5</sub>, Ca<sub>4</sub>, Mn<sub>4</sub>, Mg<sub>3</sub>, Cu<sub>2</sub>, Si<sub>1</sub>, Fe<sub>1</sub>; no. 19 (Figs. 26, 27): Hg<sub>6</sub>, Ca<sub>4</sub>, Mg<sub>2</sub>, Mn<sub>2</sub>, Fe<sub>1</sub>, As<sub>1</sub> and Hg<sub>6</sub>, Ca<sub>3</sub>, Mg<sub>2</sub>, Mn<sub>2</sub>, Si<sub>1</sub>, Fe<sub>1</sub>, As<sub>1</sub> and Hg<sub>5</sub>, Ba<sub>4</sub>, Ca<sub>3</sub>, Mg<sub>1</sub>, Mn<sub>1</sub>, Fe<sub>1</sub> and Fe<sub>6</sub>, Hg<sub>3</sub>, Al<sub>3</sub>, Si<sub>3</sub>, Ca<sub>3</sub>, Mn<sub>3</sub>, Ti<sub>2</sub>, Mg<sub>1</sub> and finally Fe<sub>6</sub>, Hg<sub>4</sub>, Si<sub>4</sub>, Ca<sub>4</sub>, Al<sub>3</sub>, Mn<sub>3</sub>, Ti<sub>2</sub>, Mg<sub>1</sub>; no. 20: Ca<sub>3</sub>, Hg<sub>3</sub>, Mg<sub>1</sub>, Si<sub>1</sub>, Fe<sub>1</sub>; no. 21 (Fig. 29): Hg<sub>6</sub>, Ca<sub>5</sub>, Mg<sub>4</sub>, Si<sub>3</sub>, Fe<sub>3</sub>, Mn<sub>2</sub>, Al<sub>1</sub>, As<sub>1</sub> and Hg<sub>6</sub>, Ca<sub>5</sub>, Mg<sub>4</sub>, Si<sub>4</sub>, As<sub>4</sub>, Fe<sub>3</sub>, Ti<sub>2</sub>, Mn<sub>2</sub>, Al<sub>1</sub> and Ca<sub>5</sub>, Hg<sub>4</sub>, Mg<sub>2</sub>, Si<sub>1</sub>, Fe<sub>1</sub>, As<sub>1</sub> and Ca<sub>5</sub>, Hg<sub>4</sub>, Mg<sub>2</sub>, Si<sub>1</sub>, Mn<sub>1</sub>, Fe<sub>1</sub>, As<sub>1</sub>; no. 22 (Figs. 31, 32): Hg<sub>5</sub>, Ca<sub>3</sub>, Ba<sub>3</sub>, Fe<sub>2</sub>, Mg<sub>1</sub>, As<sub>1</sub> and Hg<sub>4</sub>, Ca<sub>3</sub>, Fe<sub>3</sub>, Ba<sub>3</sub>, Mg<sub>1</sub>, Cr<sub>1</sub>, Pb<sub>1</sub> and Ba<sub>3</sub>, Ca<sub>2</sub>, Fe<sub>2</sub>, Hg<sub>2</sub>; no. 23 (Fig. 34) Hg<sub>5</sub>, Fe<sub>4</sub>, Ca<sub>3</sub>, Mg<sub>1</sub>, Si<sub>1</sub>; no. 24 (Fig. 36): Ca<sub>3</sub>, Hg<sub>3</sub>, and Hg<sub>4</sub>, Ca<sub>3</sub>, Mg<sub>1</sub> as well as Ca<sub>3</sub>, Hg<sub>3</sub>, Mg<sub>1</sub>; no. 25 (Fig. 39): Hg<sub>4</sub>, Ca<sub>2</sub>, and Hg<sub>4</sub>, Ca<sub>2</sub>, Mg<sub>1</sub>, As<sub>1</sub>; no. 26: Fe<sub>4</sub>, As<sub>3</sub>, Hg<sub>3</sub>, Ca<sub>2</sub>, Mg<sub>1</sub>; no. 27: Hg<sub>6</sub>, As<sub>3</sub>, Ca<sub>2</sub>, Mg<sub>1</sub>; and no. 28 (Figs. 41, 42): Ca<sub>3</sub>, Hg<sub>3</sub>.

41. Because of the low contamination in the red of a carved lacquerware object from the fifteenth century, Garner (1963) concluded that vermilion had been used. In view of the experience gained here and a study of the original analysis,<sup>2</sup> these results should not be interpreted in this way; rather they are a clear indication of the presence of natural cinnabar. Garner's reference is to a source not available to the author and which refers to the use of dry-process vermilion since the fourth century B.C. (Read 1936).

42. In no. 14 (Figs. 19–21) with Ca<sub>4</sub>, Fe<sub>4</sub>, Mg<sub>2</sub>; in no. 19 (Figs. 26, 27) with Fe<sub>6</sub>, Hg<sub>3</sub>, Al<sub>3</sub>, Si<sub>3</sub>, Ca<sub>3</sub>, Mn<sub>3</sub>, Ti<sub>2</sub>, Mg<sub>1</sub>; and in no. 26 with Fe<sub>5</sub>, Ca<sub>2</sub>, Hg<sub>2</sub>, Mg<sub>1</sub>, Mn<sub>1</sub>.

43. No. 22 (Figs. 31, 32) Ca<sub>5</sub>, Fe<sub>5</sub>, Mg<sub>2</sub>, As<sub>2</sub>, Si<sub>1</sub>, Mn<sub>1</sub>; no. 23 (Fig. 34): Fe<sub>3</sub>, As<sub>2</sub>, Ca<sub>2</sub>, Hg<sub>2</sub>, Mg<sub>1</sub>.

44. No. 1 (Fig. 5) Si<sub>5</sub>, Fe<sub>5</sub>, Hg<sub>4</sub>, Mg<sub>4</sub>, Al<sub>4</sub>, Ca<sub>4</sub>, Ti<sub>4</sub>, Mn<sub>2</sub>; no. 8 (Fig. 11): Hg<sub>4</sub>, Si<sub>3</sub>, Ca<sub>3</sub>, Mn<sub>3</sub>, Fe<sub>3</sub>, Ba<sub>3</sub>, Mg<sub>2</sub>, Al<sub>1</sub>, Ti<sub>1</sub>, Cu<sub>1</sub>; no. 12: Ca<sub>4</sub>, Ag<sub>2</sub>, Hg<sub>2</sub>; and no. 19 (Figs. 26, 27): Ca<sub>4</sub>, Hg<sub>4</sub>, As<sub>3</sub>, Mn<sub>3</sub>, Mg<sub>1</sub>, Si<sub>1</sub>, Fe<sub>1</sub>.

45. No. 14 (Figs. 20, 21) Ca<sub>4</sub>, Mg<sub>2</sub> and Ca<sub>4</sub>, Mg<sub>2</sub> as well as Ca<sub>1</sub>; no. 24 (Fig. 36) Ca<sub>3</sub>, Si<sub>1</sub> and Hg<sub>5</sub>, Ca<sub>3</sub>, Mg<sub>2</sub>, Si<sub>2</sub>, Fe<sub>2</sub> (contaminated); no. 25 (Fig. 39) Si<sub>2</sub>, Ca<sub>2</sub>, Hg<sub>2</sub>, Mg<sub>1</sub>, Fe<sub>1</sub>, As<sub>1</sub> and Ca<sub>1</sub>, Hg<sub>1</sub> as well as Hg<sub>3</sub>, Ca<sub>1</sub>, As<sub>1</sub> and Ca<sub>4</sub>, Hg<sub>3</sub>.

46. The list of evidence of mercury in black layers can be expanded to include a piece of the Jiajing era (Linden-Museum, Stuttgart, OA 20.796L; Burmester, Brandt 1982) which was not included in the series of lacquerware described in detail here.

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# The Production and Use of Chinese Raw Urushi and the Present State of Research

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**R**aw (or natural) urushi is the viscous sap of the lacquer tree, a deciduous plant six to ten meters high. The outer bark of the tree is whitish, the inside yellowish. Production of raw urushi in the People's Republic of China has developed steadily in the past ten years and has doubled as a natural resource. Two thousand one hundred seventy tons of raw urushi were produced in 1978 and production has continued to increase.

## ***Distribution of the lacquer tree and collection of sap***

Both the climate and soil of the People's Republic of China are favorable for the growth of the lacquer tree. It grows in mountainous districts between latitude 19–42° and longitude 97–126° where the annual rainfall exceeds 0.6 m and the annual mean temperature is 8–20°C. Lacquer trees grow in twenty-three provinces throughout the country, notably Shanxi, Hubei, Sichuan, Yunnan, and Guizhou. There are 161 major urushi-producing districts. The People's Republic of China leads the world in both the production and the export of urushi.

When the bark of the tree is stripped and a cut made, the milky white sap oozes out. The season for tapping varies according to the region, due to differences in climate. In areas where the temperature is slightly higher, tapping starts ten days before the summer solstice and continues until the frosts begin, a period of about 120 days. In areas where the temperature is slightly lower, it begins around the first week in July and continues until the first week of October, a period of only about ninety days. The actual period for the collection of the sap is usually determined by the growth of the lacquer tree (Local Product Bureau 1980).

Chinese urushi farmers have a long history of urushi production and have developed various methods of making the cuts, based upon their experiences. In Hubei and Sichuan we find "willow leaf" and "eyebrow" styles, in Shanxi, Yunnan, and Guizhou "Chinese character," "cattle nose," and "scissor" style cuts. For example, with the "cattle nose" style of cut, the sap is collected in a shell placed under a cut shaped like the nose of a cow. Sap is collected from a tree every two to three years, and only four or five times from the same tree.

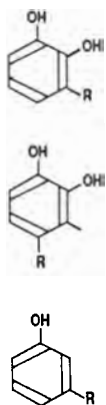
## Composition and constituents of the sap

The composition of the sap of the lacquer tree varies depending on the species of the tree and also, in the case of trees of the same species, on the place and season of collection. Table 1 shows the composition of sap collected from *Rhus verniciflua* in Maoba, Hubei province, People's Republic of China (Du 1986).

The main constituent of the sap is urushiol. The subconstituents of urushiol were investigated by Majima (1922), Dawson (Sunthankar et al. 1954), Kumanotani (Yamauchi 1982), and Tyman (1982). In recent years, high performance liquid chromatography (HPLC) and high resolution capillary gas chromatography have made such great progress that several new subconstituents of urushiol have been successfully isolated and identified. Under the guidance of Professor Kumanotani and with the cooperation of Dr. Oshima, I found that urushiol in Chinese raw urushi comprises not only those compounds having the formula in Figure 1, but also those in Figures 2 and 3; he also clarified the structure of their side chain (Du 1984, unpublished results). The results obtained are summarized in Figure 4.

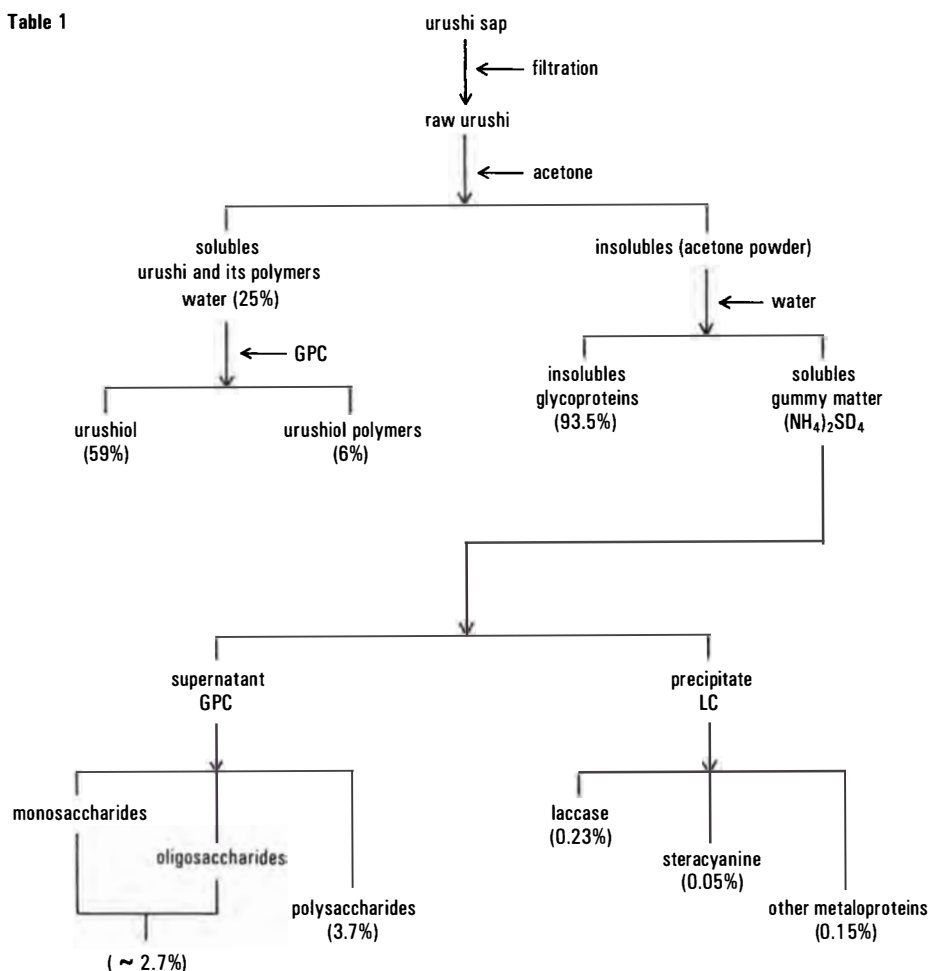
Chinese, Korean, and Japanese lacquer trees are all the same species (*Rhus verniciflua*) and their saps have exactly the same urushiol composition (very similar to that of American poison ivy except that the American plant contains fewer triene subconstituents; Elsohly et al. 1982).

Recently, I explored the chemical structure and proportion of the subconstituents of the main components of Taiwanese and Vietnamese lacquer trees (*Rhus succedanea*), laccol, and that of Thai and Burmese lacquer trees (*Melanorrhoea usitata*), thitsiol (1986). The results obtained are shown in Figures 5 and 6 in which are listed some new compounds found.



Figures 1–3. Compounds of urushiol in Chinese raw urushi.

Table 1



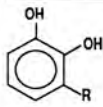
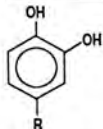
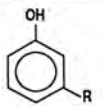
No.	R (C <sub>15</sub> , C <sub>17</sub> )	%
	1	57.5
	2	trace
	3	trace
	4	9.9
	5	8.4
	6	21.2
	7	trace
	8	2.1
	9	1.4
	10	1.2
	11	0.6
	12	
	13	2.5
	14	1.1
	15	2.3

Figure 4. Urushiol constituents of the Chinese and Japanese tree, *Rhus verniciflua*.

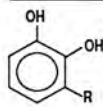
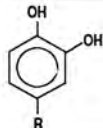
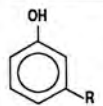
No.	R (C <sub>17</sub> , C <sub>15</sub> )	%
	1	trace
	2	0.2
	6	1.0
	6	3.5
	7	trace
	7	41.5
	8	3.2
	8	trace
	9	2.8
	10	33.8
	4	trace
		0.5
	5	1.0
	3	2.1

Figure 5. Laccol constituents of the Taiwanese and Vietnamese lacquer tree (*Rhus succedanea*).

Figure 6. Thitsiol constituents of the Thai lacquer tree (*Melanorrhoea usitata*).

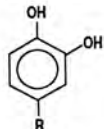
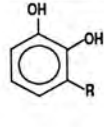
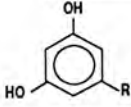
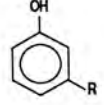
	R	%
	1a	C <sub>17</sub> H <sub>29</sub> (all <i>cis</i> )
	1b	C <sub>17</sub> H <sub>29</sub> (includes at least one <i>trans</i> double bond)
	1c	C <sub>17</sub> H <sub>31</sub> (all <i>cis</i> )
	1d	C <sub>17</sub> H <sub>33</sub> ( <i>trans</i> )
	1e	C <sub>15</sub> H <sub>29</sub> ( <i>cis</i> )
	1f	C <sub>15</sub> H <sub>31</sub>
	3a	-(CH <sub>2</sub> ) <sub>10</sub> C <sub>6</sub> H <sub>5</sub>
	3b	-(CH <sub>2</sub> ) <sub>12</sub> C <sub>6</sub> H <sub>5</sub>
	2a	C <sub>17</sub> H <sub>29</sub> (all <i>cis</i> )
	2b	C <sub>17</sub> H <sub>29</sub> (includes at least one <i>trans</i> double bond)
	2c	C <sub>17</sub> H <sub>31</sub> (all <i>cis</i> )
	2d	C <sub>17</sub> H <sub>33</sub> ( <i>cis</i> )
	2e	C <sub>17</sub> H <sub>33</sub> (possibly <i>trans</i> )
	2f	C <sub>15</sub> H <sub>29</sub> ( <i>cis</i> )
	2g	C <sub>15</sub> H <sub>31</sub>
	5a	-(CH <sub>2</sub> ) <sub>10</sub> C <sub>6</sub> H <sub>5</sub>
	5b	-(CH <sub>2</sub> ) <sub>12</sub> C <sub>6</sub> H <sub>5</sub>
	4a	-(CH <sub>2</sub> ) <sub>10</sub> C <sub>6</sub> H <sub>5</sub>
	4b	-(CH <sub>2</sub> ) <sub>12</sub> C <sub>6</sub> H <sub>5</sub>
	6a	C <sub>17</sub> H <sub>31</sub>
	6b	-CH <sub>2</sub> CH(OH)C <sub>17</sub> H <sub>31</sub>
	6c	-CH <sub>2</sub> CH(OH)C <sub>17</sub> H <sub>29</sub>
	6d	-(CH <sub>2</sub> ) <sub>10</sub> C <sub>6</sub> H <sub>5</sub>
	6e	-(CH <sub>2</sub> ) <sub>12</sub> C <sub>6</sub> H <sub>5</sub>
	6f	-CH <sub>2</sub> CO(CH <sub>2</sub> ) <sub>10</sub> C <sub>6</sub> H <sub>5</sub>
	6g	-CH <sub>2</sub> CO(CH <sub>2</sub> ) <sub>12</sub> C <sub>6</sub> H <sub>5</sub>
	6h	-(CH <sub>2</sub> )CH(OH)(CH <sub>2</sub> ) <sub>12</sub> C <sub>6</sub> H <sub>5</sub>

Figure 7. Chromatograms of urushiol and laccol from the sap of (a) *Rhus verniciflua* (Shensi, The People's Republic of China) and (b) *Rhus succedanea* (Taiwan) in the underivatized form. Conditions: column, methylsilicone, 12.5 m x 0.2 mm i.d.,  $df = 0.33$  m; column programmed from 23C (maintained for 8 min) to 28C at 5C/min; injection- and detector temperature 28C; carrier gas (helium) linear velocity 40 cm/sec; splitting ratio 50:1. Numbers on peaks represent compound numbers; the peak marked with an arrow was not identified.

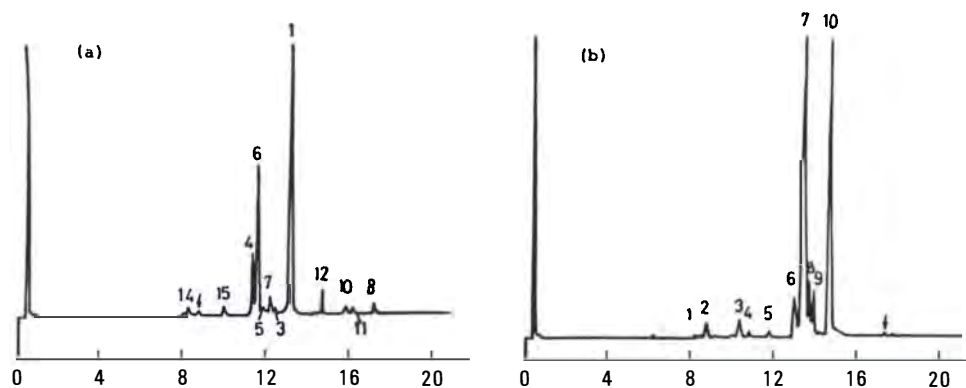


Table 2

Compound*	China						Japan		
	Hupei	Shenst	Huxian	Fengju	Songya	Kiangs	Yamagata	Naruko	Ibaraki
1	64.13	53.72	53.84	57.37	59.37	38.49	51.30	60.75	57.24
3	—	0.32	—	—	—	0.42	0.19	0.23	0.35
4	2.86	9.66	24.80	12.88	13.08	2.82	14.49	10.75	5.21
5	0.85	1.47	0.50	0.65	—	2.80	1.03	1.23	1.50
6	23.01	25.51	12.61	19.08	12.54	47.18	25.03	19.33	25.82
7	3.06	3.55	2.02	2.45	1.94	3.90	3.13	3.25	4.35
8	0.59	0.47	2.11	1.79	6.51	0.29	0.57	0.56	1.00
10	1.32	0.72	0.85	1.37	1.99	0.28	0.71	0.33	0.27
11	0.18	0.39	0.64	0.52	0.78	—	0.27	—	1.25
12	1.19	2.05	1.77	2.29	1.94	0.51	2.45	1.90	0.90
Monomer content (%)	88.6	77.9	83.8	75.8	80.8	—	90.9	92.6	—

\*Compounds 1, 8 and 12 contain compounds 2, 9 and 13 respectively, as trace contaminants.

Table 3

Number	Analysis					Average $\pm$ S.D.
	1	2	3	4	5	
1	0.165	0.147	0.153	0.161	0.172	0.160 $\pm$ 0.009
2	0.990	0.982	0.963	0.935	0.969	0.968 $\pm$ 0.019
3	2.143	2.186	2.206	2.192	2.163	2.178 $\pm$ 0.022
4	0.465	0.425	0.473	0.481	0.492	0.467 $\pm$ 0.023
5	0.984	0.961	0.978	0.954	0.963	0.986 $\pm$ 0.011
6	3.531	3.602	3.556	3.541	3.582	3.562 $\pm$ 0.026
7	41.499	41.508	41.704	41.829	41.756	41.672 $\pm$ 0.151
8	3.163	3.212	3.186	3.201	3.154	3.183 $\pm$ 0.022
9	2.772	2.706	2.689	2.690	2.714	2.714 $\pm$ 0.030
10	33.771	33.051	33.647	33.893	33.465	33.571 $\pm$ 0.295

So far, separation and analysis of mixed phenolic compounds in natural urushi have been conducted by gas chromatography (GC) or liquid chromatography (LC) after being converted into their methylated (Craig et al. 1978; Baer et al. 1980) or acetylated (Yamauchi et al. 1980) derivatives. I used HPLC and capillary gas chromatography for quantitative analysis of the subconstituents of urushiol without modifying them and found that phenolic subconstituents could be separated directly from natural urushi. This direct method is expected to play a great part in the analysis of phenolic subconstituents of urushiol, its uses, the synthesis of derivatives, tests for its sensitivity to the human body and immunotherapy.



Figure 8. Chromatograms of the oily component of the sap from the Thai lacquer tree (*Melanorrhoea usitata*) in the underivatized form. Conditions: column, methylsilicone, 12.5 m x 0.2 mm i.d.,  $df = 0.33$  m; column programmed from 25°C (maintained for 1 min) to 30°C at 5°C/min (d); injection-port and detector temperature 300°C; carrier gas (helium) linear velocity 36 cm/sec; splitting ratio 50:1. Numbers represent compounds; peaks with an arrow were not identified, and that with an asterisk is due to phthalate from a plastic container.

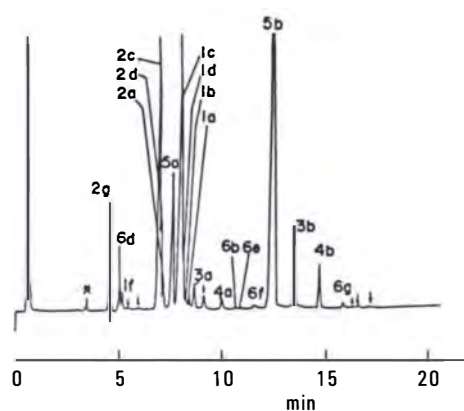


Table 4

Number	Compound	Analysis						Average $\pm$ S.D.
		1	2	3	4	5	6	
1	2g	3.773	4.101	3.983	3.968	3.863	3.768	3.909 $\pm$ 0.132
2	6d	1.120	1.638	1.124	1.364	1.511	1.493	1.375 $\pm$ 0.214
3	1f	0.620	0.879	0.632	0.663	0.759	0.841	0.734 $\pm$ 0.110
4	2c	21.051	20.585	20.688	17.699	17.701	20.550	19.712 $\pm$ 1.568
5	5a	7.173	7.178	8.292	7.467	7.863	7.212	7.531 $\pm$ 0.458
6	1c	20.111	20.162	20.441	20.560	21.210	20.259	20.457 $\pm$ 0.406
7	1a	0.638	0.616	0.899	0.647	0.969	0.600	0.728 $\pm$ 0.162
8	3a	1.062	1.076	1.197	1.130	1.244	1.059	1.128 $\pm$ 0.078
9	4a	0.622	0.705	0.675	0.729	0.705	0.708	0.691 $\pm$ 0.004
10	6f	0.346	0.361	0.342	0.400	0.326	0.334	0.352 $\pm$ 0.003
11	5b	36.305	35.025	34.795	37.777	36.181	35.689	35.962 $\pm$ 1.075
12	3b	3.562	3.638	3.531	3.733	3.684	3.633	3.630 $\pm$ 0.007
13	4b	2.035	2.124	2.066	2.178	2.151	2.110	2.104 $\pm$ 0.005

### Assessment of the quality of raw urushi

According to Kumanotani (1983), when it is allowed to stand in the air, raw urushi that contains urushiol with a readily oxidizable catechol nucleus and olefinic side-chain is oxidized enzymatically in its polymerizable urushi phase to produce oxidized films having a lower density of cross-linkages. It is believed, therefore, that the quality of a given raw urushi depends mainly on the content of urushiol triene subconstituents and the amount and activity of enzyme. The composition of raw urushi has been scientifically verified by conventional methods in combination with the chromatographic technique that we have developed.

As mentioned above, the urushiol in Chinese urushi does not differ from that in Japanese urushi as to subconstituents and composition. Both have a large content of triene subconstituents (Du 1984) and are readily dried (Fig. 7a and Table 2).

Laccol in Taiwanese and Vietnamese urushi unexpectedly contains much monoene subconstituent (Du n.d.), though it also contains triene constituents. These urushi are said to be poor in drying, which is partly attributable to their insufficient triene content (Fig. 7b and Table 3).

Thai urushi contains a compound having the interesting structure in Figure 9 in an amount of about 38% (Du 1985). Since the compound has no triene-b bearing side-chain, Thai urushi is very difficult to dry. However, it has been found that the compounds of Thai urushi can be used as a new material for the chemical industry by isolating them from the sap (Fig. 8 and Table 4).

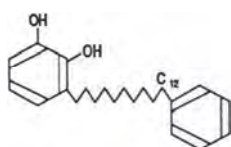


Figure 9. Thai urushi compound.

Recently, I also successfully developed a method for the rapid analysis of metalloprotein enzyme in natural urushi by HPLC, resulting in good reproducibility and accuracy (Du n.d.). Samples of raw urushi were taken to Japan from the People's Republic of China for the 1985 Urushi Study Group and analyzed there in detail. Both the quantity and the activity-level of oxidized enzyme in raw urushi were measured and it was found that Chinese urushi contained more oxidized enzyme, and that it was also more active. Therefore it may be said that Chinese urushi is better.

**Table 5**

Place of production	China <sup>a</sup>					Taiwan	Japan <sup>b</sup>			
	Hupei	Shenei			Kiamgei	Ibaraki	Naruko	Slowly dried urushi		
		Pingli	Langquan	Songya					Huxian	
Peak area (mg)	13.04	12.9	19.3	15.9	14.3	5.2	17.4	13.1	8.8	9.1
Activity	54.68	45.2	67.3	50.0	26.4	7.4	21.0	12.2	6.7	10.0
Specific activity (activity/peak area)	4.19	3.5	3.49	3.15	1.85	1.42	1.21	0.93	0.76	1.10

<sup>a</sup> Urushi obtained in China in 1982 and Taiwan in 1979.

<sup>b</sup> Urushi obtained in Japan in 1979.

### **Present uses of urushi**

Raw urushi has been used in China for more than six thousand years. It has been employed as a coating for objects in everyday use, works of art, and industrial equipment. It has also been found that urushi on ancient items unearthed from tombs thousands of years old still retains its vivid luster and incomparable durability.

Raw urushi and lacquer coating materials are characteristically hygienic, water repellent, hard wearing, and good insulators. Factories processing raw urushi in the People's Republic of China produce three types of urushi: traditional, purified, and improved. Traditional urushi is used for wood furniture, laboratory benches, and flooring. Purified and improved urushi are used as industrial coating materials. At present, more than twenty kinds of these urushi are produced and extensively used (Training Course 1976).

Raw urushi is also used in the spinning, printing, chemical, and petroleum industries, in gravel production, mining, production of Chinese lacquerware, as a coating for the bottoms of ships and boats, and for the repair of ancient buildings. For example, pipes used for extracting crude oil formerly required cleaning every day to remove deposits on their inner walls, but a single application of improved urushi coating material gives such excellent results that now the walls can be kept clean for at least three months. Marine growth on the hulls of ships immersed in seawater for prolonged periods, results in corrosion. But it has been found that application of improved urushi prevents such growths, thus maintaining the sailing speed and prolonging the life of the ship. It is also a good coating material for undersea cables.

Recently, a great many Chinese researchers have been engaged in developing new applications for both raw urushi and improved urushi. Urushi has been repeatedly examined for toxicity and verified nontoxic. Consequently, it can be used as a coating material for the inner walls of water tanks and cans to store fresh water, soy sauce, sake, vinegar, and so on. Hardened films of improved urushi were applied to the inner walls of a chimney two hundred meters high and six meters in diameter; they exhibited no change upon testing for thermal stability at 15°C and they resisted 5% solutions of nitric acid, hydrochloric acid, and potassium hydroxide, and a 20% solution of sulfuric acid.

**Future urushi research  
in the People's  
Republic of China**

In the People's Republic of China today, scientific research into urushi has made many advances in addition to the development of processes for and the increase in the quantity of the production of raw urushi. A special urushi research program has been organized and a Chinese Society of Urushi Chemistry has been established. National meetings and cooperation on urushi research have also been arranged. Study groups have been organized, with Wuhan University playing a leading part on the academic side and the Xian Raw Urushi Institute representing the urushi industry (Kenjo 1982). There are also some local institutes. In the past, raw urushi in was investigated mainly by the lacquer industry, but now many researchers from various specializations—chemistry, macromolecular science, physics, enzymology, botany, medicine, pharmacology, and archaeology—are taking part. Research is being conducted in various aspects, including the growth, breeding, and biological morphology of lacquer trees; the chemistry of urushi; the scientific examination of urushi works of art; various applications of raw urushi; and the prevention and treatment of hypersensitivity to urushi.

Although synthetic coating materials are developing all the time, they have not replaced urushi and its unique qualities. It is believed that raw urushi will be further developed as a renewable coating material, whose many colors, nontoxicity, and quick-drying properties are equivalent to those of synthetic coating materials.

At the present time, saturated urushiol-30-crown-10 which is synthesized from urushiol, is being used as a potassium ion selective electrode of the highest quality (Yu et al. 1982). In addition, saturated urushiol polymers have relatively high thermal stability, with a thermal decomposition temperature reaching 30°C, (Huang et al. 1984), and can be used as a stationary phase in chromatography and as ion-selective membranes for chromatography.

Hardened urushi is believed to have anticarcinogenic properties. "P235 pinxiaopin" produced in the People's Republic of China are herbal tablets with dried urushi as the active principle. The tablets have been shown to reduce tumors in patients with cancers of the lung, stomach, and esophagus, inhibiting the growth of cancer cells and thus prolonging the lives of the patients. This medicine has won great popularity in the People's Republic of China and elsewhere.

Recent research into allergens (for allergy to Chinese urushi) has shown that an urushiol subconstituent, six-membered, unsaturated-lactone (see Fig. 10) can also be an allergen that may possibly play a part in the treatment and prevention of hypersensitivity to raw urushi. It is believed that there will be splendid results from urushi research in the near future.

Finally, I hope that raw urushi will attract the attention of many researchers to its complex and versatile properties, and that it will continue to be widely developed both for general use and for specialized processes.

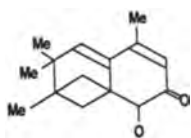


Figure 10. An urushiol sub-constituent: six-membered, unsaturated-lactone.

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# X-ray Radiography in the Study of Oriental Lacquerware Substructures

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1. H el ene Gillette was an intern from the State University College at Buffalo, New York, working in 1985-86 under Ms. Milam (1975-85 Los Angeles County Museum of Art, 1986 to present J.Paul Getty Museum) on this project at both the Los Angeles County Museum of Art and the Getty, but Ms. Gillette was not part of the Urushi Study Group.

Interest in the substructural characteristics of urushi developed during the 1985 meeting of the Urushi Study Group in Japan. There is little or no information on the subject of urushi substructures published in English. During visits to the Shosoin in Nara, the Tokyo National Museum, and the Tokyo National Research Institute of Cultural Properties, the Study Group participants examined x-ray radiographs of urushi objects and discussed the substructural characteristics of the objects, but arrived at no definitive conclusions.

In 1983 the Los Angeles County Museum of Art (LACMA) Conservation Center began a comprehensive interdepartmental project to study and examine the pieces in LACMA's extensive urushi collection. We recorded our visual and microscopic findings with photographs and written documentation. X-ray radiography was used to examine the substructures of the LACMA pieces and pieces from the Detroit Institute of Arts (DIA); the Freer Gallery of Art, Smithsonian Institution, Washington, D.C. (FGA); and the Asian Art Museum of San Francisco, Avery Brundage Collection (AAM). We are especially indebted to the staff of these institutions for sharing their information with us.

Oriental lacquerwares are made from the sap of the tree, *Rhus verniciflua*, refined and colored with various inorganic and some organic pigments. This refined sap or lacquer is applied in thin coats on a substructure. There are many core materials used for the substructure: wood, leather, cloth, paper, shell, ceramic, horn, fish skin, etc. There is very little published about these substructures, how they are manufactured, and what materials are used.

X-ray radiography is a tool that facilitates a visual reading of substructural construction as well as later additions, alterations, and repairs. Specific construction methods are repeatedly seen in the radiographs, but we do not yet have enough information to determine if these patterns are representative of a particular period or culture. In this report, we have catalogued the characteristic details seen in over one hundred radiographs of Oriental lacquerwares with wood substructures, as follows:

1. The entire substructure can be fabricated from a single piece of wood (LACMA M.53.12). A variation of this would be a single piece of wood forming the central section with added handles, feet, sides, and/or foot ring (LACMA L.78.25.6).
2. The substructure of the central base can be fabricated from the following types of jointed wood sections (Shosoin 1975:154): (a) parallel sections of wood with

2. A rub or rubbed joint is used to join two pieces of wood edge to edge. The edges are planed true, coated with adhesive and rubbed together to make a firm joint.



Figure 1 a-c. Construction of central base.



Figure 2. Coiled wood strips.

with rub joints (Fig. 1a),<sup>2</sup> (b) parallel sections of wood with rub joints and a single perpendicular butt joint (Fig. 1b), (c) parallel sections of wood with rub joints and two perpendicular butt joints (Fig. 1c).

These types of construction for the central base can be mechanically joined by dowels, cleats, split bamboo canes, fabric saturated with urushi, and/or with urushi used as an adhesive.

The single butt style of joinery may have been used to control distortion in Oriental lacquerware due to changes in relative humidity (RH) and/or poorly seasoned wood. Strengthening one side with a single perpendicular butt joint (LACMA M.78.121.1) would not necessarily control distortion; however, this would be achieved by introducing a second perpendicular butt joint on each side (AAM BL.77.M.19a.b and LACMA M.78.71.la.b).

Visual and x-ray radiographic examination were used in determining the above variations in style of joinery. Visual examination generally shows that the urushi coating buckles or cracks perpendicular to the grain of the wood substructure. Major cracks are observed to be parallel to the rub joints between the wood sections and splits in the wood.

3. Coiled wood strips can be used to form the flared sides of Oriental lacquerware (Fig. 2). The sides are formed by a series of bent wood or bamboo strips laminated or tied together. Once the wood strips are tightly fitted together, they are carved or sanded to form the sides. This makes it easy to construct round, flaring forms and also helps to counteract warpage (Shosoin 1975:148-154; AAM BL.77.M.19a.b and LACMA L.78.25.6).

4. Basket weave of reeds, grasses, or bamboo can be used to form the sides and sometimes the entire substructure of an object. This is a variation on the wood substructure. The basket weave was also used as a design element or texture on Oriental lacquerwares. Judging from the objects we have observed, this is not as durable as a wood substructure (LACMA M.78.121.9).

5. Reinforcements such as wood dowels, cleats, and split bamboo canes were used for joining and strengthening the wood substructure of the base in urushi pieces. Wood dowels and cleats are seen in some radiographs. Split bamboo canes are used as exterior supports for the wood substructures. They are adhered with urushi and/or fabric (LACMA M.78.121.9).

6. Score lines that appear to be associated with the wood substructure are radiographically opaque. There is no visible evidence of these lines on the urushi surface (LACMA L.78.19.10 and L.78.25.6) and their purpose is not known. Woodworkers score wood either to align sections during gluing or to position a pattern for tracing a design. However, many of the radiographs of Oriental lacquerware show score lines totally out of alignment or following no visible pattern (FGA 65.25).

7. The centering point was made by a sharp instrument or resulted from turning the bowl on a lathe. The centering point usually appears opaque in the radiograph. This opacity could be due to a buildup of *sabi* (urushi mixed with pulverized ceramic, clay, or rice flour) in the indentation (LACMA M.78.121.1). Occasionally the centering point appears as a dark spot in the radiograph. This could be due to the type of *sabi* material used or even to the lack of a *sabi* layer.

8. Various metal strips, sheets, or wires were used to reinforce the rim, foot, or edges of urushi (AAM BL.77.M.40a.b). Wire was also used to tie together the coiled wood strips and bundles of reed, grass, or bamboo in basket weave pieces (LACMA M.78.121.9, M.79.182.6, and M.80.96.2).

9. Grouting, probably *sabi*, was used as a filling material in the wood substructure (AAM BL.77.M.19a.b).

10. Fabric, probably a bast fiber textile, was used in the dry lacquer technique as a substructure (FGA 68.67). In wood substructures, fabric was sometimes



used to hold the wood sections together and to reinforce the rim and the foot ring. In addition, fabric was used to give tooth or texture to the subsequent urushi layers (LACMA M.78.25.7 and M.80.96.2; AAM BL.77.M.19a.b).

11. Restorations in urushi are visible as dark areas or occasionally as light areas in the radiographs. These areas differ from the original urushi because of the different pigments and resins used in the repair (LACMA M.78.121.1).

X-ray radiography was used to examine the substructures of lacquerwares with wooden substructures. Radiography produces a shadowgraphic image created by the interaction of x-rays with an object. X-rays can be absorbed, transmitted, or scattered, depending on the materials present in the object. The equipment used at LACMA was a General Electric M01/CE5 x-ray tube that emits fairly low energy x-rays. The radiographs were done by direct exposure onto Kodak Industrex M film, a very sensitive, high contrast film. Extensive testing was done to determine the kilovoltage (kV) and milliamperage (mA) required to show various structural details.

During our study, we found that Oriental lacquerwares pose some unique problems in achieving sharp, high contrast x-ray radiographic images. Organic materials commonly used in Oriental lacquerware, such as urushi itself, wood, carbon black, and fabric are very x-ray transparent. These wares require low kVs of 20–35 and mAs around 5, with short time-exposures of about one minute. However, most red urushi and some multicolored urushi have very x-ray opaque pigments incorporated in the urushi. These pigments include litharge (lead oxide), orpiment (yellow arsenous sulfide), realgar (orange arsenic sulfide), ochers (iron compounds), and vermilion (mercuric sulfide; e.g. LACMA M.53.12). Lacquerwares containing these x-ray opaque pigments require higher kVs around 40–45 and longer time-exposures of 2–5 minutes, with the mA remaining at 5 (5 is the highest mA setting on the LACMA Radiation Source or x-ray tube). Note that lead screens are not used with settings below 200 kV.

Carved Oriental lacquerwares present other problems. They can be either red, solid black, or alternating layers of red and black, or three or more colored layers of urushi carved to varying depths. These urushi pieces are very high contrast subjects, with x-ray transparent and x-ray opaque areas. Since each of these areas would require different energy levels or the use of filters to achieve detail in all areas, multiple x-ray radiographs or multiple x-ray exposures on a single film sheet can give satisfactory results.<sup>3</sup>

Once the quality of contrast and density in the x-ray radiographic image is clear and legible, the various components of the lacquerware substructure can be observed. The dark areas in the radiograph are formed by x-ray transparent materials in the urushi lacquerware. The lighter areas in the radiograph are formed by the more x-ray opaque materials.

Reading of the radiograph can be complicated by the fact that light or opaque areas can sometimes be the result of overlapping or differing thicknesses of components within the object. The shadowgraphic depiction of carved urushi is a good example (LACMA L.78.19.10 and M.80.96.1; FGA 65.25). X-ray opaque images such as score lines, centering points, grouting, and worm holes can be caused by a build-up of fill material (*sabi*). Because of the pulverized ceramic contained in the *sabi*, it is more x-ray opaque than wood or textile.<sup>4</sup>

3. "To insure proper density for multiple kV exposures, the total amount of exposure (mAs) required for the most satisfactory single kV radiograph is proportionally divided among the different kVs according to the empirically derived formula  $mAs=K/(kV)^2$ ." (Kushel 1984:5); see also Rawlins 1937:38-39.

4. The x-ray radiograph when viewed in stereo may reveal on which side of the urushi substructure the centering point and/or score lines are inscribed (see for example, FGA 67.14, Fig.6).

Radiographs reveal areas of additions, alterations and repairs as they generally have different densities due to the different resins and/or pigments used in these restorations. Also, they will sometimes reveal inscriptions or design motifs that are covered by later layers of urushi, if x-ray opaque pigments were used in these motifs.

Metal reinforcements can also be distinguished in an x-ray radiograph. Metals are among the most x-ray opaque materials, therefore they appear as light areas in the radiographic image.

The following lacquerware x-ray radiographs were chosen to illustrate structural characteristics. It should be noted that in these examples the substructural characteristics are from various periods and cultures.

Figure 3. Wine cup with winged handles, Chinese, Eastern Zhou dynasty; height 3.2 cm, width 16.5 cm, depth 15 cm; Los Angeles County Museum of Art M.83.147, gift of Donald and Iris Blackmore. Cups of this type are found in tombs excavated around Changsha, Hunan province.



The black urushi was applied over a wood substructure, then decorated with designs in red urushi along the mouth, rim, and handles. Rapid change in relative humidity after excavation deformed the handles and caused the wood substructure to shrink. Many surviving examples of these cups are known to have been excavated from a waterlogged environment. When the objects are moved to an environment with lower relative humidity, the wood undergoes cellular collapse and shrinks across the grain.

Technical data: 35 kV, 5 mA, 3 minutes, distance from tube 90 cm. The light area in the center is a repair. The painted geometric design in cinnabar urushi is also light in the radiograph.

Another example of a similar substructure with the wood grain running side to side as opposed to lengthwise is FGA 47.24.

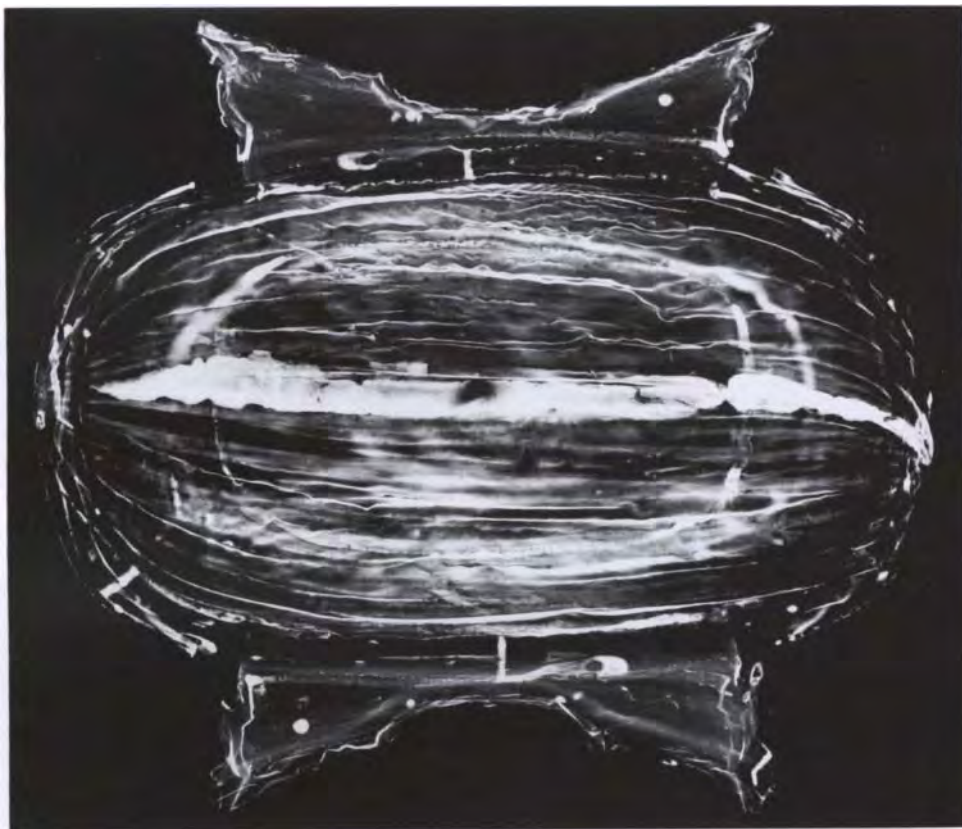


Figure 4. Shallow bowl, Chinese, Han dynasty (early second century B.C.); height 3.5 cm, width 21.9 cm; Los Angeles County Museum of Art M.53.12, Mr. and Mrs. Allan C. Balch Fund.

The wood substructure is fabricated from a single piece of wood and is covered with a thin base coat of dark ocher-colored urushi. Motifs of whorls, "C" shapes, and spirals in thin red urushi decorate the bowl. There is no *sabi* layer between the wood substructure and the fragile urushi layers. The urushi surface has buckled and cleaved from the substructure, particularly along the wood grain and the edges of the bowl.

Technical data: 40 kV, 5 mA, 1 minute, distance from tube 90 cm. The designs in red urushi are visible in the radiograph. Repairs are visible as light areas along the rim of the bowl.



Figure 5. Six-lobed dish in the shape of a mallow flower, Chinese, Southern Song dynasty; height 3.8 cm, width 15.9 cm; Los Angeles County Museum of Art L.78.25.6, collection of Mr. and Mrs. John H. Nessley.

The six overlapping carved petals that form the side have a raised undulating edge. The wood substructure is coated with transparent and opaque brown urushi. The inscription in red urushi is painted within the circular foot ring and is visible as a light area in the radiograph. The urushi surface is damaged along the rim. There are cracks and small losses along the sides. Within the circular foot ring, the urushi surface has major cracks running in a cross pattern.

Technical data: 30 kV, 5 mA, 1 minute, distance from tube 90 cm. The central base appears to be constructed from a single wood section. The side is constructed of coiled wood strips. A coarse fabric is applied over the wood substructure. There is a centering point and an open crosshatched pattern of fine score lines. The foot ring is off center.

Other examples of Oriental laquerware with similar substructures are LACMA M.83.148.2, chrysanthemum dish, Chinese, Ming dynasty (sixteenth century); DIA 79.148, chrysanthemum dish, Chinese, Song/Yuan dynasty (thirteenth century); LACMA M.80.212, tray with multi-lobed rim (chrysanthemum), Chinese, Ming dynasty.

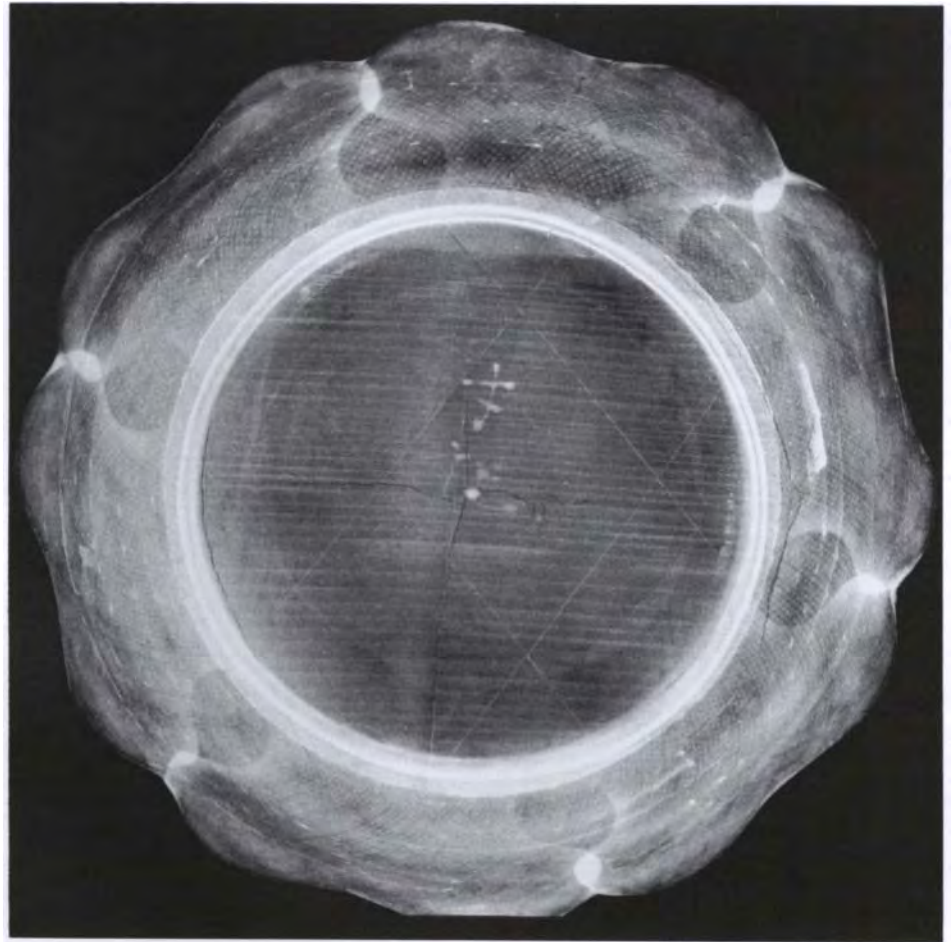
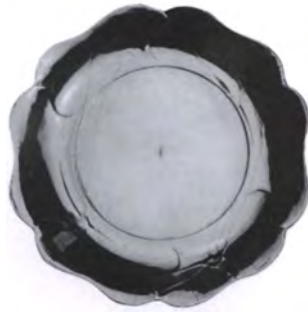


Figure 6. Circular tray, attributed to Chinese, Song dynasty (c. A.D. 960–1279); height 4.1 cm, width 31.8 cm; Los Angeles County Museum of Art M.78.121.1, gift of Mr. and Mrs. Eric Gilberg.

The wood substructure is covered with *sabi*, fabric, and several layers of urushi. The interior of the tray is red urushi. The rim is accented with black urushi, and the underside is decorated with strips of bamboo that radiate out toward the rim. The urushi has parallel and perpendicular cracks. Separation of the wood sections caused the parallel cracks, while the swelling and contraction of the wood sections caused the perpendicular cracks. The outer rim has several radial cracks; the sides of the tray have horizontal cracks that parallel the underlying coiled wood strip construction. The urushi surface is cleaving away from the *sabi* layer along the major cracks.

Technical data: 45 kV, 5 mA, 1 minute, distance from tube 90 cm. The substructure is composed of parallel wood sections with a single perpendicular butt joint. Coiled wood strips from the sides. Faintly visible is the fabric reinforcement of the foot and the rim. There is a centering point and four faint score-lines in the central section. Repairs are visible as dark areas in the center and the rim and light areas along the side.

A similar example of this wood substructure is LACMA M.82.135, circular platter, Chinese, Yuan dynasty.

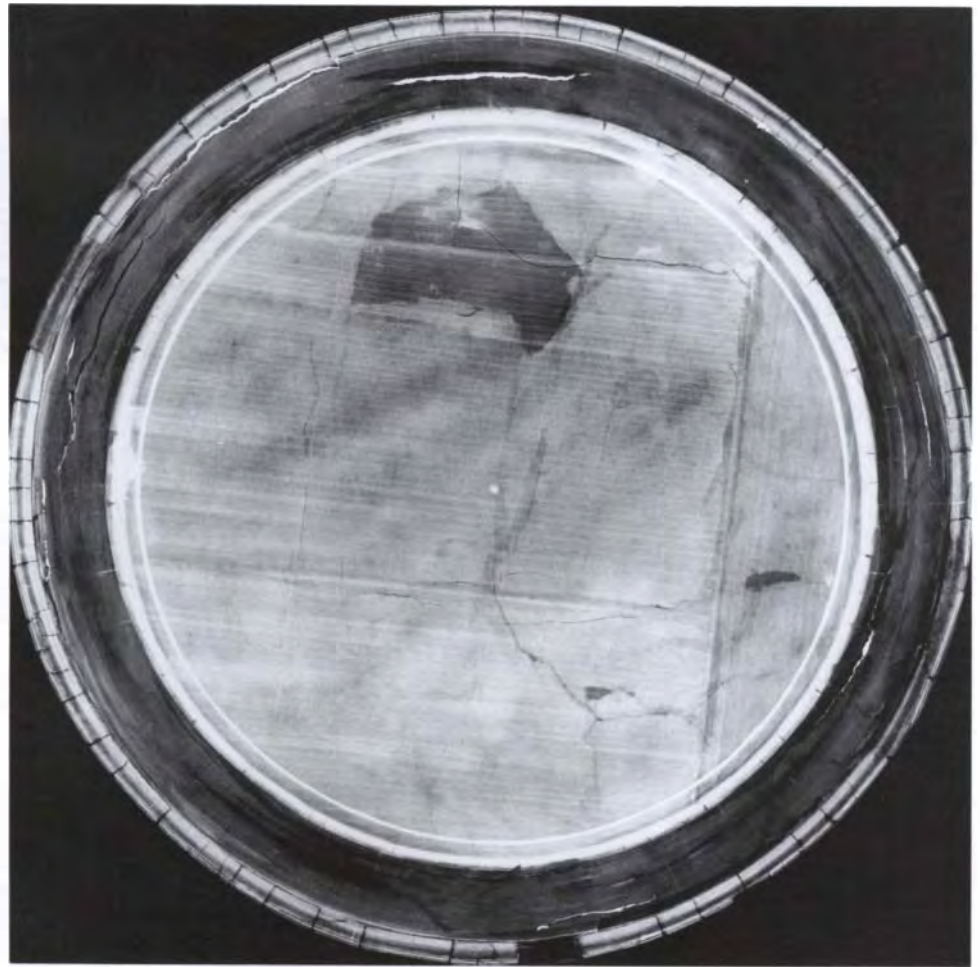


Figure 7. Pair of lobed dishes, Chinese, Song dynasty (c. A.D. 960-1279); height 1.9 cm, width 12.7 cm; Asian Art Museum of San Francisco, Avery Brundage Collection, BL.77 M.40a and b, formerly in the collection of Jean-Pierre Dubosc, lent to the Asian Art Museum by the Christensen Fund.

Technical data: 40 kV, 7 mA, 30 seconds, distance from tube 65 cm. The central base of each dish appears to be constructed of a single wood section. The sides of both dishes are constructed of coiled wood strips. Both dishes have x-ray opaque centering points and score lines. There is a double set of score lines inscribed in the upper dish. The rim of both dishes is reinforced with a metal strip.

Other examples of metal strip used as a rim reinforcement are FGA 67.14, lobed dish, Chinese, Song dynasty, and DIA 79.145 and 79.146, two red urushi dishes in the shape of a mallow flower, Chinese, Southern Song dynasty.

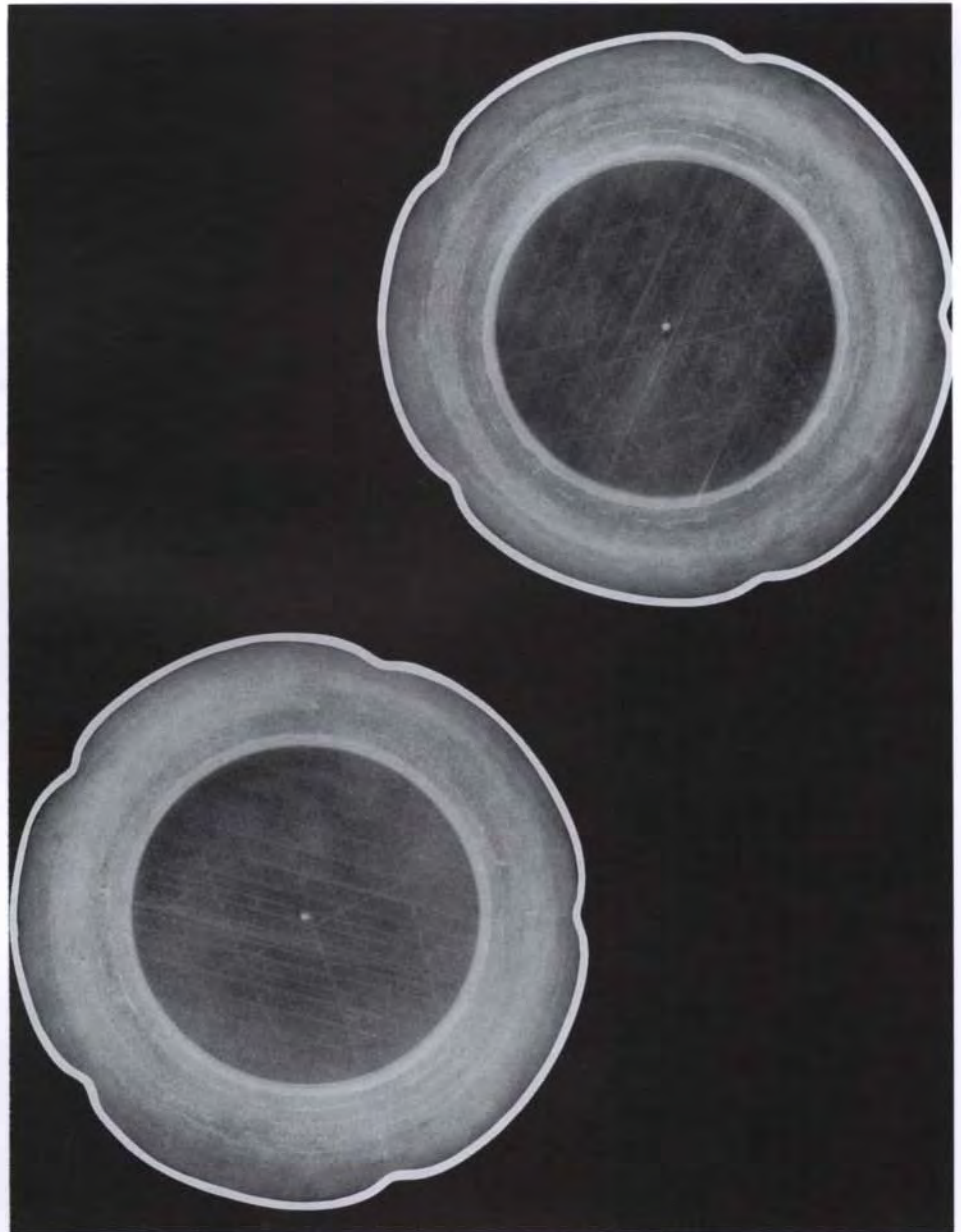


Figure 8. Dish with five-lobed base, cavetto, rim, and foot, Chinese, Song dynasty; height 4.3 cm, width 19.5 cm; courtesy of the Freer Gallery of Art, Smithsonian Institution, Washington, D.C. 67.14.

Technical data: 20 kV, 3 mA, 3 minutes, distance from tube 90 cm. Five planks of wood form the central base. Score lines are present in the base in an open crosshatched pattern. Coiled wood strips form the five-lobed side. A metal strip reinforces the rim and foot ring. The centering point and the areas between the coiled wood strips contain x-ray dense *sabi* material.

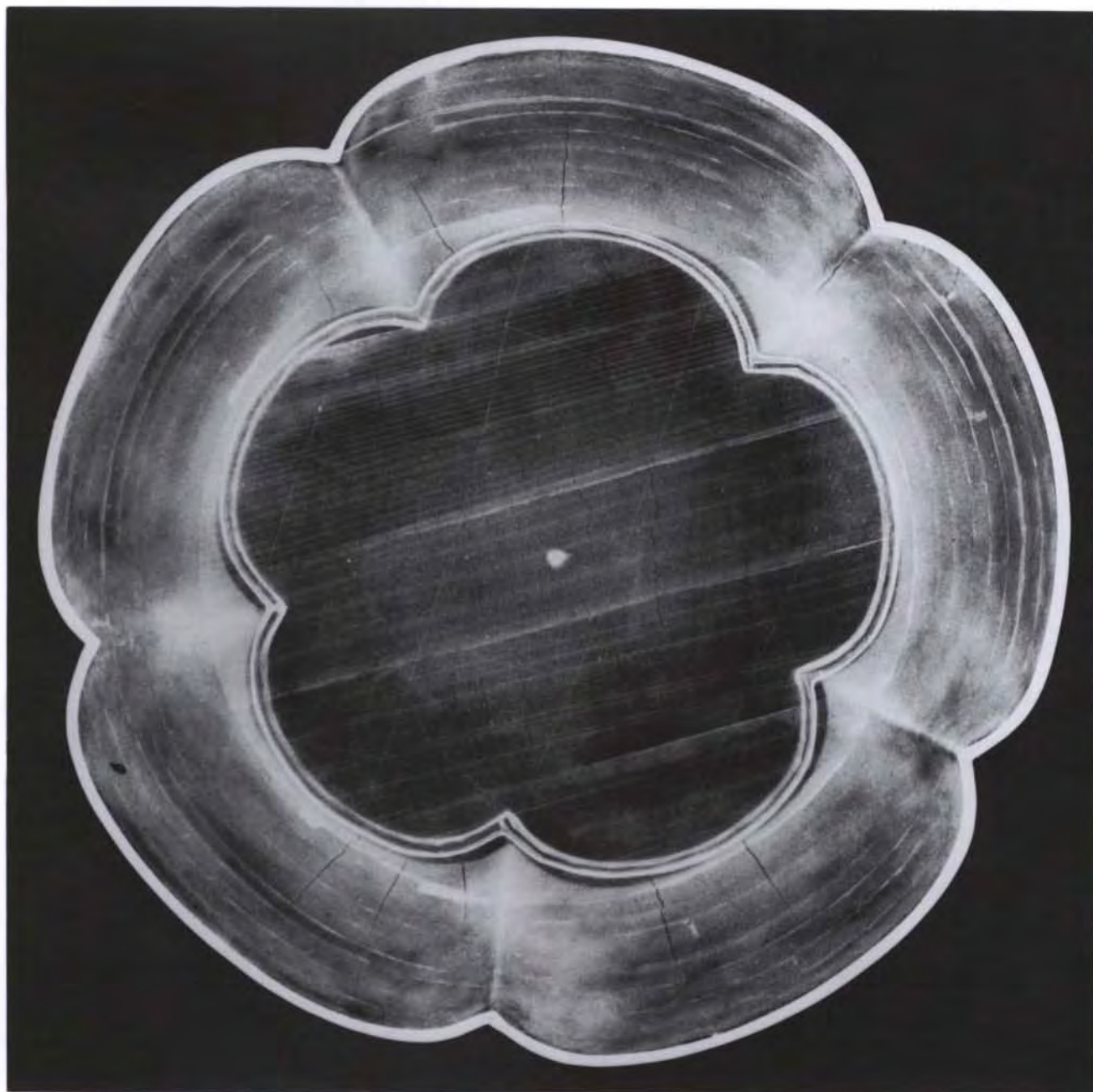




Figure 9 (see Fig. 8).

The details illustrated here are an enhanced stereo pair of x-ray radiographs of the central area of the Freer Gallery of Art lobed dish 67.14. Since the details were made from the radiographs by contact printing, the values are reversed from normal radiographs. The x-ray opaque areas such as the centering hole and score lines appear dark here. Cracks show up as white lines.

If a stereo viewer is not available, the stereo image can still be seen by placing a 75 mm x 125 mm file card or suitable piece of cardboard vertically on one's nose at a right-angle to the face; the left eye will see only the left image and the right eye will see only the right image. The muscles of the eyes must be relaxed to make the eyes converge by prolonged staring at one fixed spot (such as the centering point or a crossing of the score lines), or by raising the eyes to a distant object and then gazing back at the paper without refocusing.

When stereo fusion is achieved, a three-dimensional structure will be perceived. The score lines can be seen to lie below the cracks, in the uppermost layer of the wood. The urushi layer on the bottom of the piece (inside the foot ring) can be distinguished because it contains small, x-ray opaque dots, probably *sabi*. The centering point appears to be below the surface. Since the radiograph was taken with the bowl base down on the x-ray film, the centering point and score lines are on the underside of the plate in this example.

Technical data: 30 kV, 5 mA, 3 minutes, distance from tube 100 cm, 900 mAs; Film Kodak Type M, ready pack, normal development. Enhanced stereo pair taken with the tube 15° off vertical to the left and right.

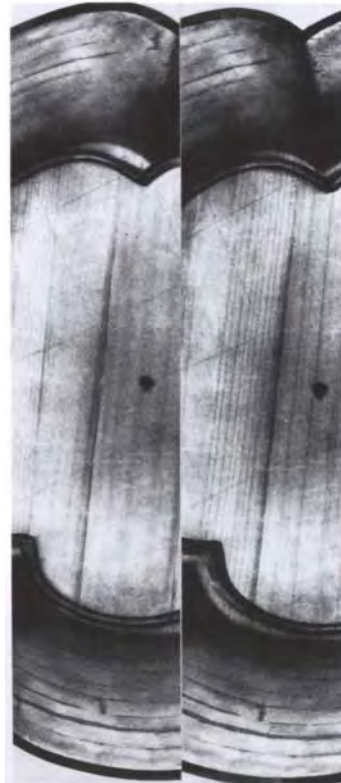


Figure 10. Circular platter, Chinese, Yuan dynasty (fourteenth century); height 3.4 cm, width 27.6 cm; Los Angeles County Museum of Art M.82.135, gift of the Sammy Yu-Kuan family in honor of his eightieth birthday.

The black urushi is carved in a pattern of sword-pommel scrolls. A symmetrical arrangement of spirals and arcs is carved in the center of the platter. The underside of the rim is carved in a pattern of shorn sword-pommel scrolls. The base within the foot ring has been coated with layers of black urushi. Major cracks and small losses run along the crevices in the carved urushi design. The *craquelure* within the foot ring of the base is not perpendicular to the grain of the wood substructure. This condition could have resulted from a later reinforcement of the base with fabric and urushi.

Technical data: 40 kV, 5 mA, 1 1/2 minutes, distance from tube 90 cm. The base is built of wood sections that have a single perpendicular butt joint. The rim is constructed from coiled wood strips. The wood substructure is covered with fabric. There are three small restorations visible as light areas near the 10, 11 and 1 o'clock positions. There is a centering point.

Another example of this substructure is LACMA M.78.121.1, circular tray, Song dynasty (c. A.D.960–1279).



Figure 11. Tray with cranes and chrysanthemums, Yuan dynasty (fourteenth century); height 3.5 cm, width 29.2 cm; Detroit Institute of Arts 80.25, Founders Society purchase, Stoddard Fund for Asian Art.

Black urushi tray carved with cranes and chrysanthemums, with a *xiangcao* border of arabesque scrolls.

Technical data: 45 kV, 5 mA, 4 minutes 10 seconds, distance from tube 90 cm. The base is constructed of parallel wood sections with a single perpendicular butt joint. The sides are constructed from coiled wood strips. The entire substructure is reinforced by coarsely woven fabric. There is a centering point and other dense splotches (possibly insect or worm holes filled with *sabi*).

Another example of a similar wood substructure is LACMA M.81.92, tray with two flying peafowl among peonies, Chinese, Yuan dynasty.

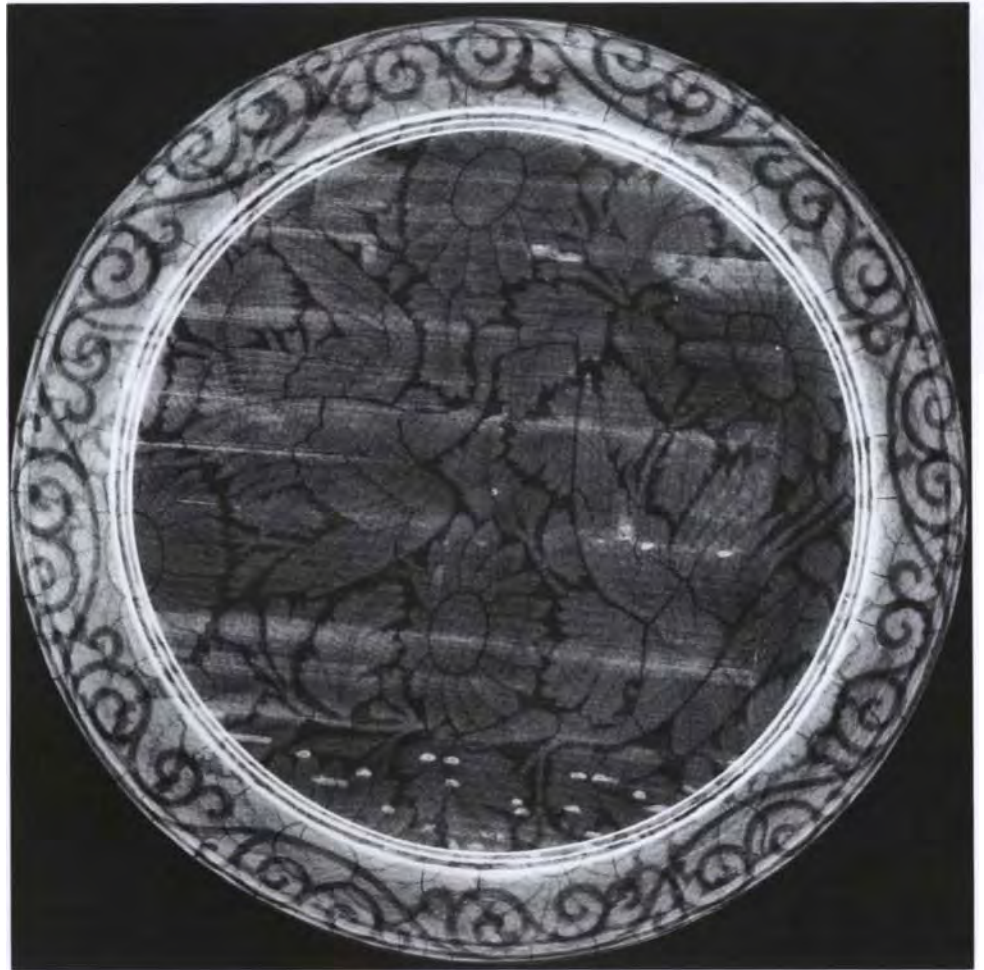


Figure 12. Dish with flattened foliated rim, Chinese, Yuan dynasty (first half of fourteenth century); height 2.8 cm, width 21.6 cm; courtesy of the Freer Gallery of Art, Smithsonian Institution, Washington, D.C., 68.67.

Technical data: 20 kV, 3 mA, 3 minutes, distance from tube 60 cm. The substructure of the dish appears to be only fabric, with no visible wood elements. The dish was manufactured in the dry lacquer technique, where fabric saturated with urushi is stretched over a form. The cracks in the urushi appear to be random.

The dry lacquer technique was used to form the sides of many urushi bowls. An example of this is LACMA M.83.148.2, chrysanthemum dish, Chinese, Ming dynasty (sixteenth century).

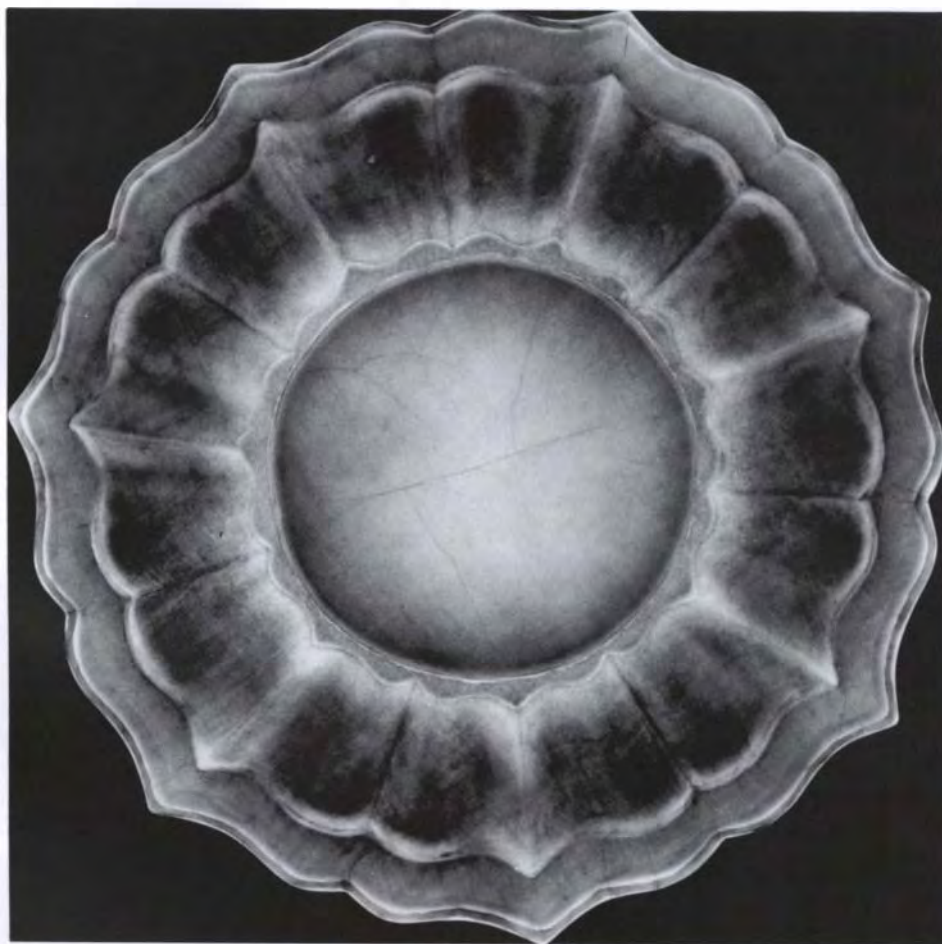


Figure 13. Black lobed box with painted decoration, Chinese, Yuan or early Ming dynasty (fourteenth-fifteenth century); height 7.6 cm, width 15.6 cm; Asian Art Museum of San Francisco, Avery Brundage Collection BL 77 M.19a and b.

Technical data: 40 kV, 7 mA, 30 seconds, distance from tube 65 cm. The central sections of both the lid (Fig. 12a) and the base (Fig. 12b) are constructed from parallel wood sections with two perpendicular butt joints. There is fabric reinforcement extending over the entire wood substructure. Several bent wood strips are laminated together to form the eight-lobed sides. *Sabi* used as grouting is visible as light areas between the wood strips.

Examples of this lobed side construction are: DIA 80.49, red and black urushi dish with a design of prunus-blossom, Chinese, Yuan dynasty; LACMA M.80.154, carved red urushi five-lobed dish, Chinese, Yuan dynasty; LACMA L.82.19 collection of Mr. Irwin Jaeger, five-lobed dish, Chinese, Ming dynasty; LACMA M.78.70, lobed food-box, Chinese Qing dynasty (eighteenth century).



Figure 14. *Chrysanthemum dish, Ming period (sixteenth century); height 3.2 cm, width 27.9 cm; Los Angeles County Museum of Art M.83.148.2, gift of Mr. and Mrs. John H. Nessley.*

The dish is red urushi with a painted urushi vine motif over the fluted border. The back of the dish is black. A major crack in the urushi surface runs along the joint of the base and the rim. There are fine parallel cracks on the base of the dish.

Technical data: 40 kV, 5 mA, 1 minute 15 seconds, distance from tube 90 cm. The base is constructed of parallel wood sections. Fabric starts at the edge of the central wood substructure and continues to the edge of the fluted rim. There is no evidence of coiled wood strip construction. The type of damage along the rim and the lack of a coiled wood substructure suggests that it could be a dry lacquer construction. There are faint score lines through the central substructure, and a visible centering point.

Another example of this substructure is DIA 79.148, chrysanthemum dish, Chinese, Song/Yuan dynasty (thirteenth century).

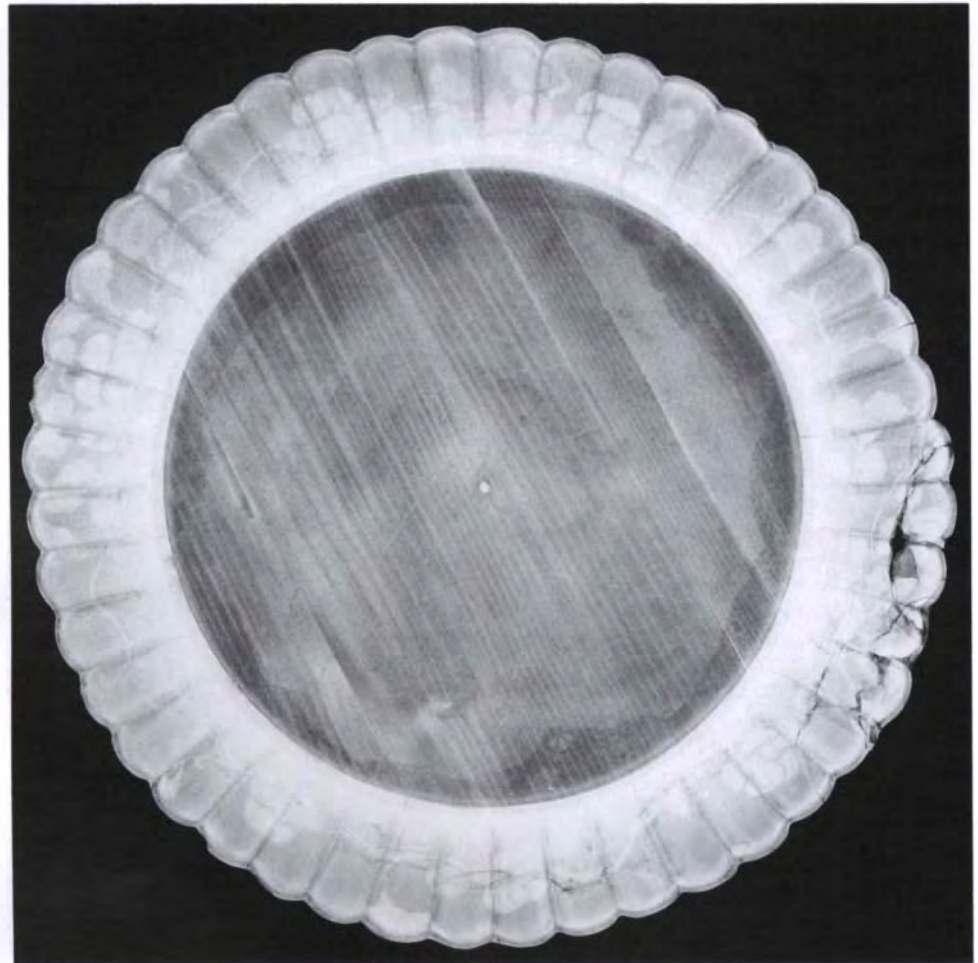


Figure 15. Octagonal box, Chinese, Ming dynasty (fifteenth century); height 12.1 cm, width 26.7 cm; Los Angeles County Museum of Art M.80.96.2 a and b, gift of Dr. and Mrs. Michael Robert Terk.

Black urushi with *raden* (mother-of-pearl inlay) design. The copper reinforcing wire is visible through the urushi. The thinly applied urushi layer has a distinct *craquelure* that is perpendicular to the grain of the wood substructure.

Technical data: 40 kV, 5 mA, 2 minutes 15 seconds, distance from tube 90 cm and 100 cm. The central area of both the lid (Fig. 14a) and the base (Fig. 14b) is constructed with parallel wood sections. Several wood strips are laminated to form the eight sides of the lid and the base. The wood substructure is covered with fabric. A two-ply twisted copper wire is used to reinforce the edges as a decorative motif.

Other examples of this side construction and use of wire reinforcement are LACMA M.82.207, octagonal multi-tiered box, Chinese, Yuan dynasty, and AAM BL 77 M.9, octagonal box, Chinese, Yuan to early Ming dynasty (fourteenth-fifteenth century).

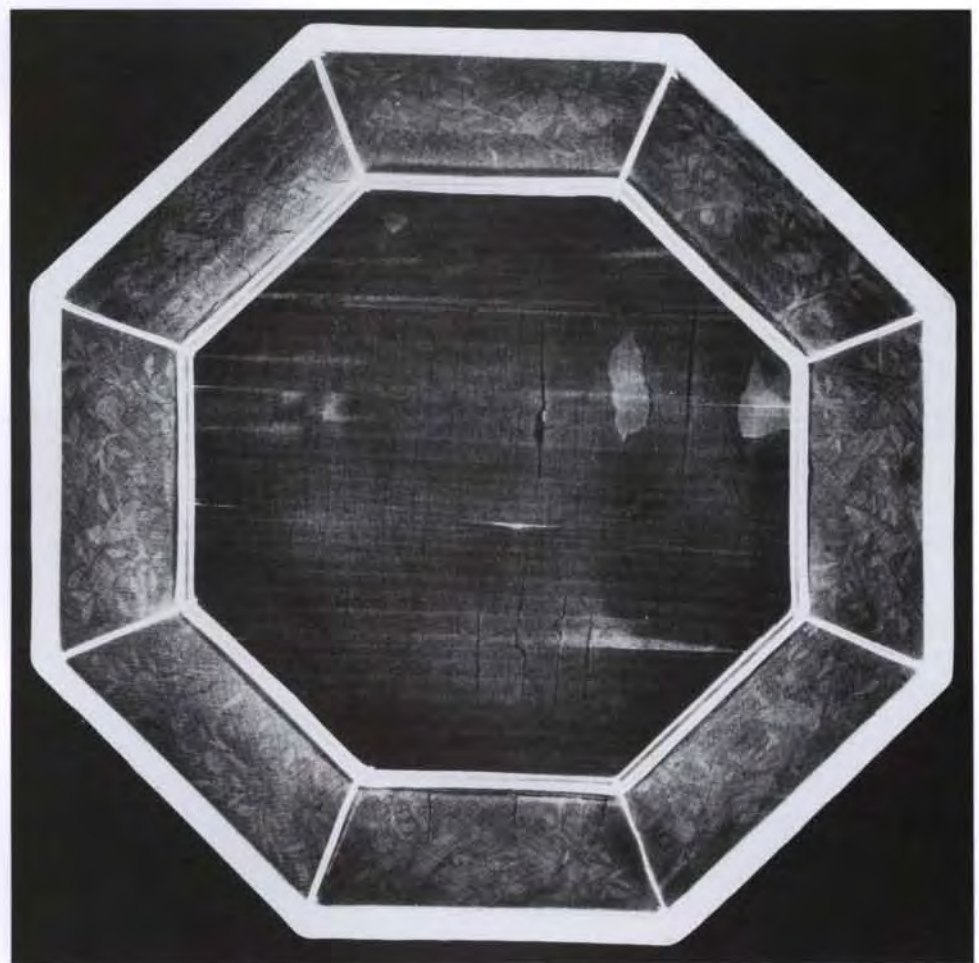
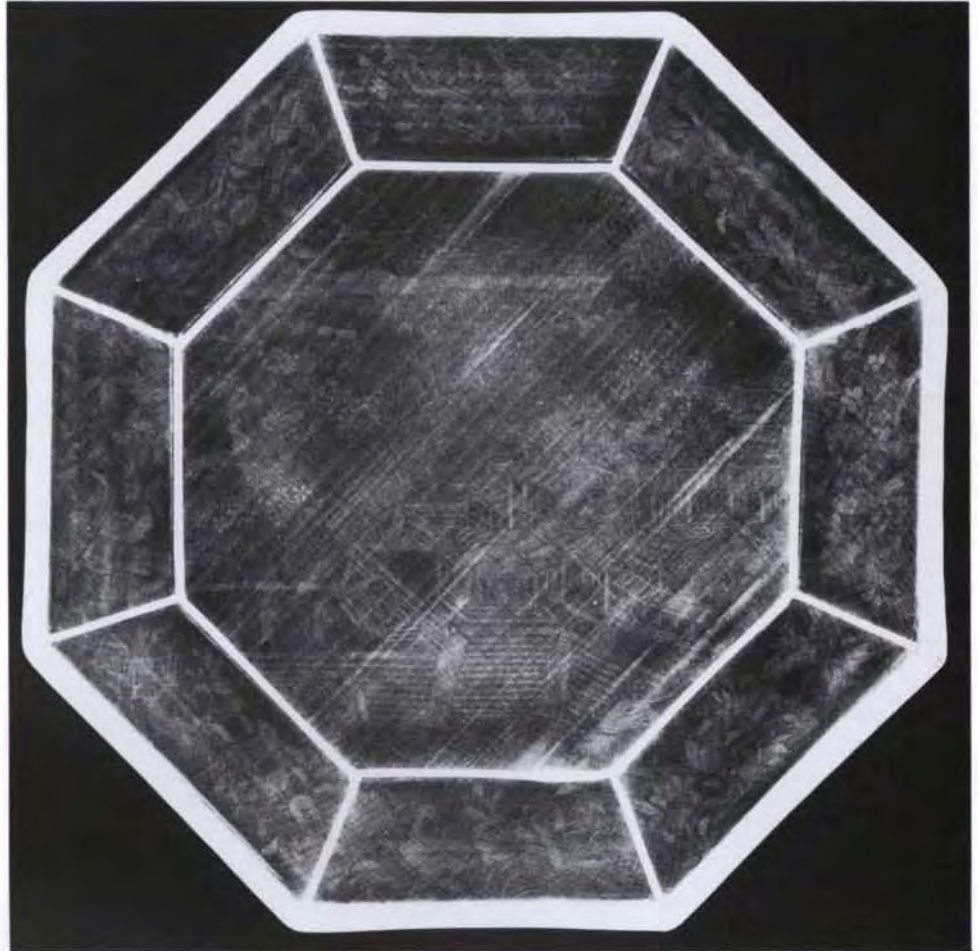


Figure 16. Tray with multi-lobed rim (chrysanthemum blossom), Ming dynasty (sixteenth century); height 6 cm, width 38.4 cm; Los Angeles County Museum of Art M.80.212, gift of Mr. and Mrs. Richard M. Baker.

The side of the tray is carved with concave grooves. The red urushi field is painted with a green and gold design of four lions around a central green disk. The surface of the tray is abraded. The urushi layers have a fine *craquelure*. There are associated losses of urushi down to the *sabi* layer.

Technical data: 40 kV, 5 mA, 1 minute, distance from tube 90 cm. The sub-structure of the central base has parallel wood sections, with coiled wood strips forming the side. There is a visible centering point and fabric reinforcement. The central circle is distinct and it has a different *craquelure* from the green and gold urushi.

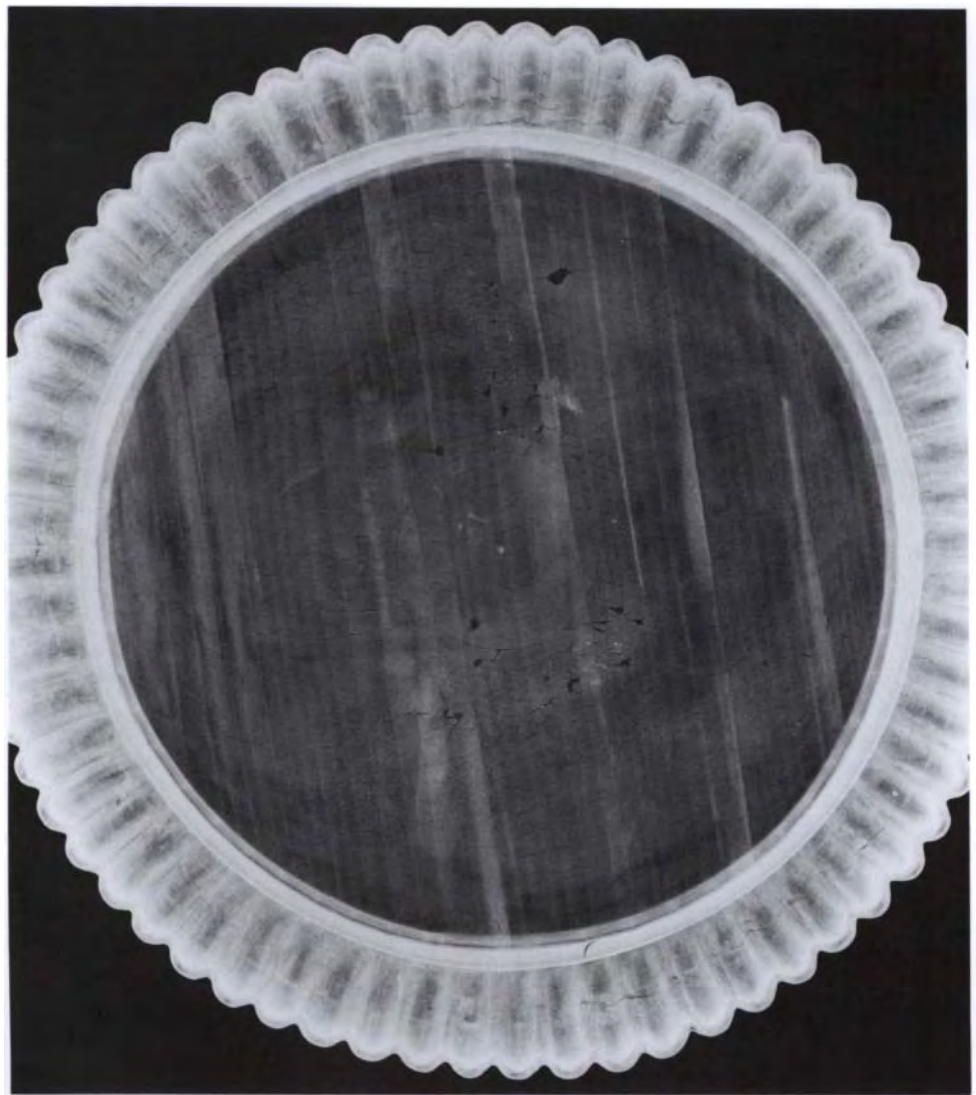




Figure 17. Square dish with two peafowl in flight, Chinese, Ming dynasty; height 3.8 cm, width 27.9 cm; Los Angeles County Museum of Art L.78.19.10, collection of Mr. H.K. Lee.

The deep carving of the black urushi reveals a ground of ocher-colored urushi. The underside is carved in a *xiangcao* pattern of arabesque scrolls. Two Chinese characters are painted with red urushi on a highly polished black background within the foot ring. The urushi layer is in good condition with a pattern of fine cracks parallel to the underlying wood sections. There are major cracks following the carved motif on the obverse of the dish.

Technical data: 45 kV, 5 mA, 2 minutes, distance from tube 90 cm. Two exposures revealed different characteristics of fabrication used in this dish. The less exposed radiograph illustrated here shows that the central base is constructed from parallel wood sections with a single perpendicular butt joint. Also visible is an open crosshatched pattern of score lines and a faint image of fabric. The x-ray radiograph clearly illustrates the Chinese characters painted on the urushi surface. The denser radiograph more clearly illustrates the construction of the four-lobed sides, where several wood strips are laminated. Fabric is used to reinforce the sides. Also note the shadow-graphic image in the radiograph caused by the different thicknesses of the carved urushi layer.

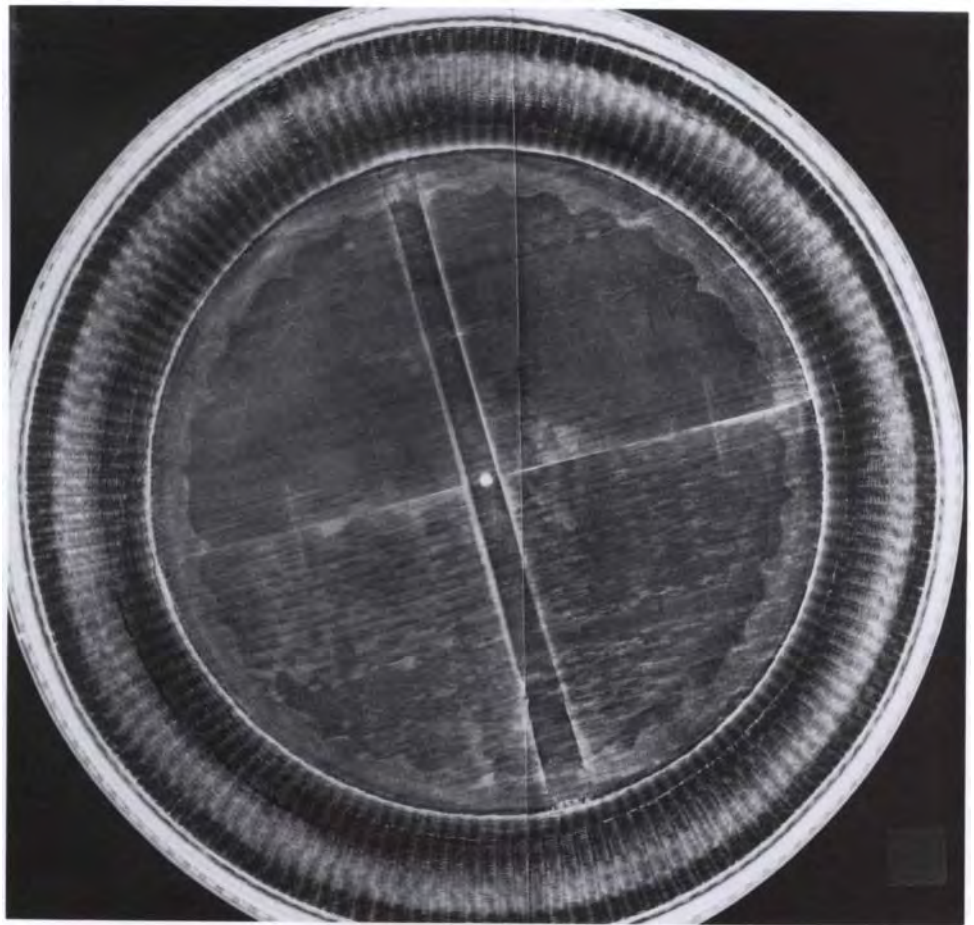


Figure 18. Circular food-box, Chinese, Ming dynasty (1635); height 21.6 cm, diameter 41.9 cm; Los Angeles County Museum of Art M.78.121.9 a and b, gift of Mr. and Mrs. Eric Gilberg.

The lid of the box is decorated with a spray of peonies painted in red and green urushi outlined in gold on a black background. The sides are basket weave covered with transparent urushi. The urushi surface has a *craquelure* that is perpendicular to the underlying wood substructure. Major cracks in the urushi run parallel to the joints of the wood sections.

Technical data: 40 kV, 5 mA, 21/2 minutes, distance from tube 100 cm. The central areas of the lid (Fig. 17a) and the base (Fig. 17b) are constructed of two wood sections that are internally doweled, and externally bridged with split bamboo canes. Centering points are cut into the bamboo strips. Fabric covers both the bamboo strips and the wood sections. Basket weave with fabric reinforcement is attached to the circumference of the wood substructure of both the lid and the base. Pieces of wire are used to bunch wood strips in both the foot ring, the rim of the base, and the rim of the lid.

Other examples of mechanical reinforcements such as dowels, cleats, bamboo, and wire to join and strengthen the wood substructures used in basket weave pieces are: LACMA M.78.121.3, oblate box, Chinese, Southern Song or Yuan dynasty, gift of Mr. and Mrs. Eric Gilberg; LACMA M.78.121.14, circular tray, Chinese, Qing dynasty (dated 1754).



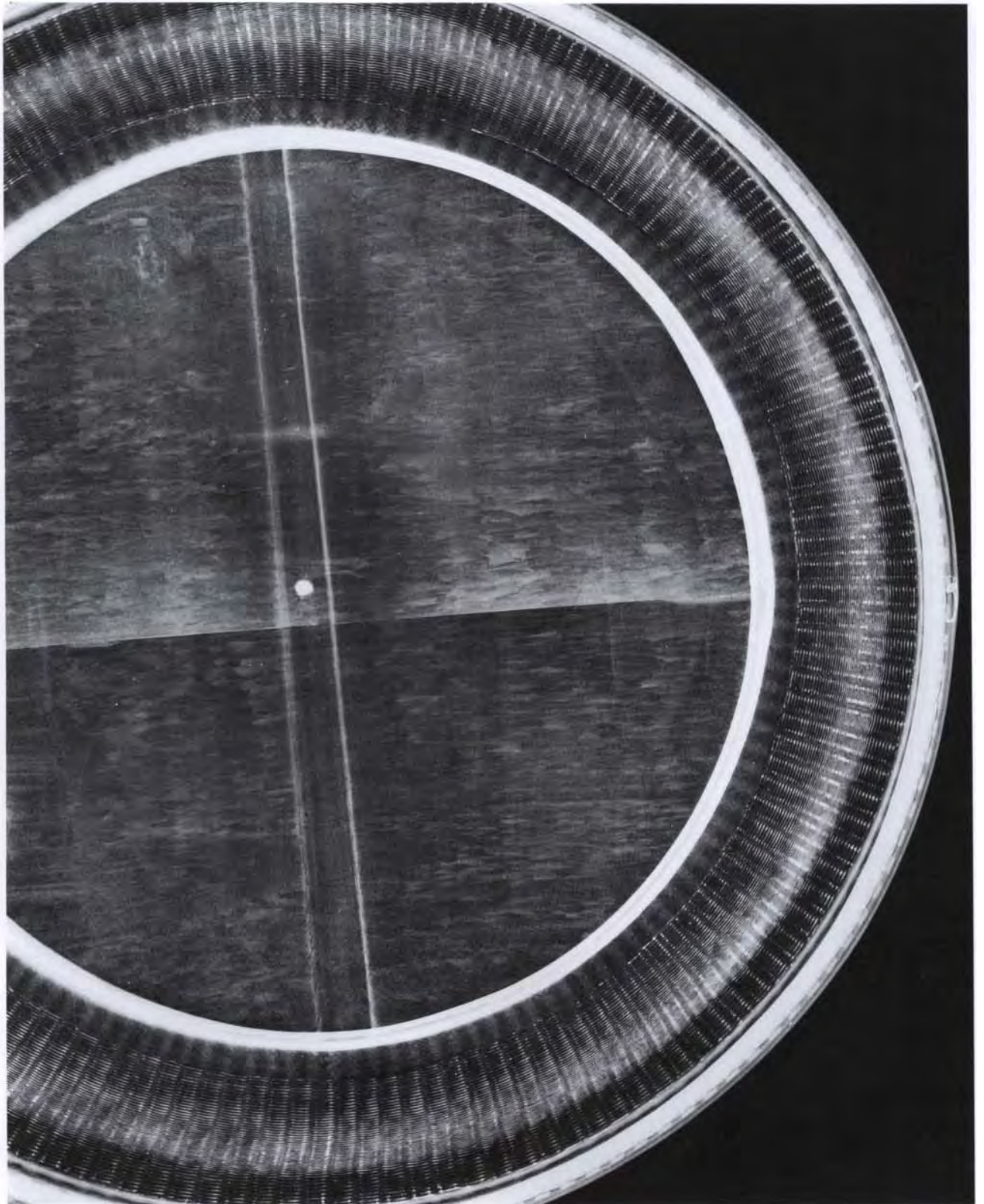


Figure 19. Round covered box, Chinese, Ming dynasty (fifteenth century); height 3.8 cm, width 11.0 cm; courtesy of the Freer Gallery of Art, Smithsonian Institution, Washington, D.C., 65.25.

Technical data: 30 kV, 5 mA, 7 minutes, distance from tube 120 cm. The central base is constructed of parallel wood sections. There are discontinuous score lines through the wood sections, which could have been scrap pieces left over from another object. The shadow image of the carved urushi illustrates the different thicknesses and densities of the urushi layers.

Another example of discontinuous score lines is AAM BL 77 M.25 a and b (Avery Brundage Collection), round box with carved floral decoration, Chinese, late Yuan dynasty (A.D. 1279–1368).

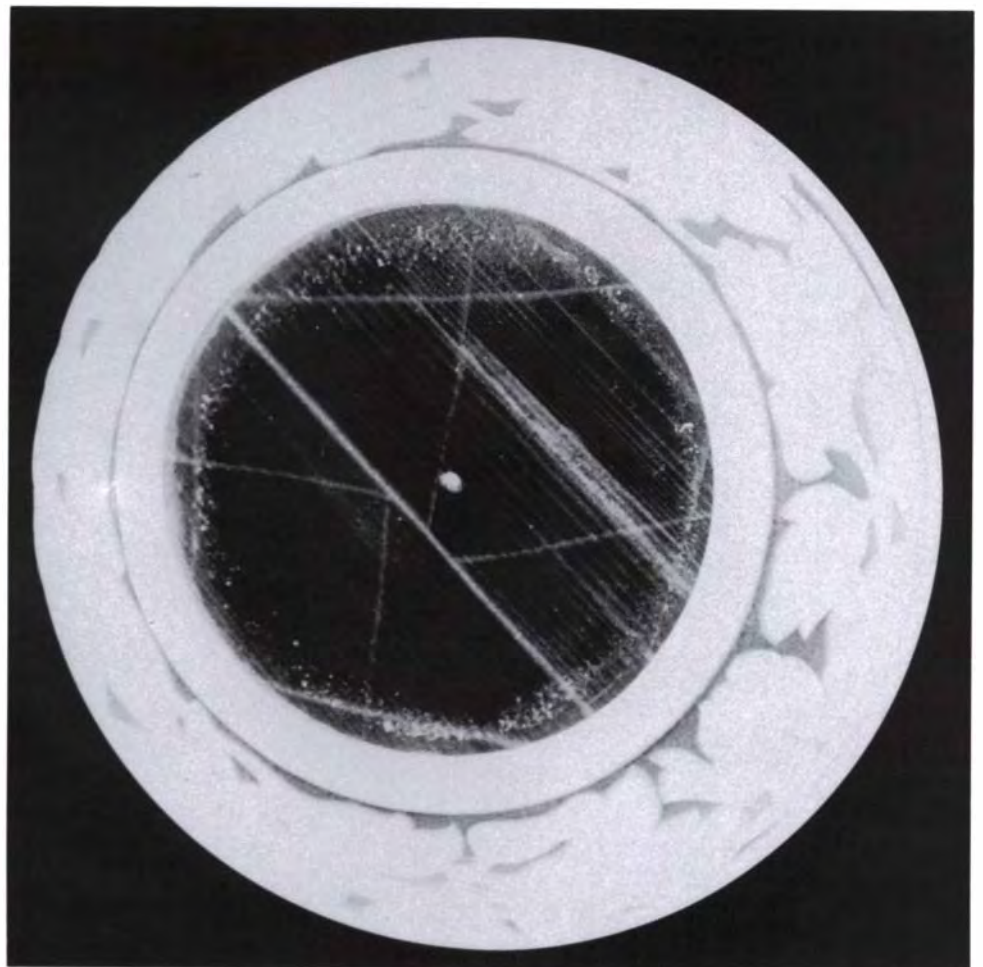


Figure 20. Circular footed tray, Ryukyu (eighteenth century); height 4.5 cm, width 22.6 cm; Los Angeles County Museum of Art M.80.109.2, gift of Mr. and Mrs. Leo Krashen.

Red urushi tray decorated with qiangjin (incised gilt lines). The thin layer of urushi is cracked along the edge of the central section.

Technical data: 40 kV, 5 mA, 1 minute, distance from tube 90 cm. The central base is constructed of three parallel wood sections, with a single perpendicular butt joint. The side is constructed from coiled wood strips. A centering point is visible. There is wire reinforcement along the join of the foot ring.

Chinese examples of similar wood substructures are: LACMA M.81.92, tray with two flying peafowl among peonies, Yuan dynasty; DIA 80.25, black urushi tray carved with cranes, chrysanthemums and a *xiangcao* pattern of arabesque scrolls, Yuan dynasty (fourteenth century).

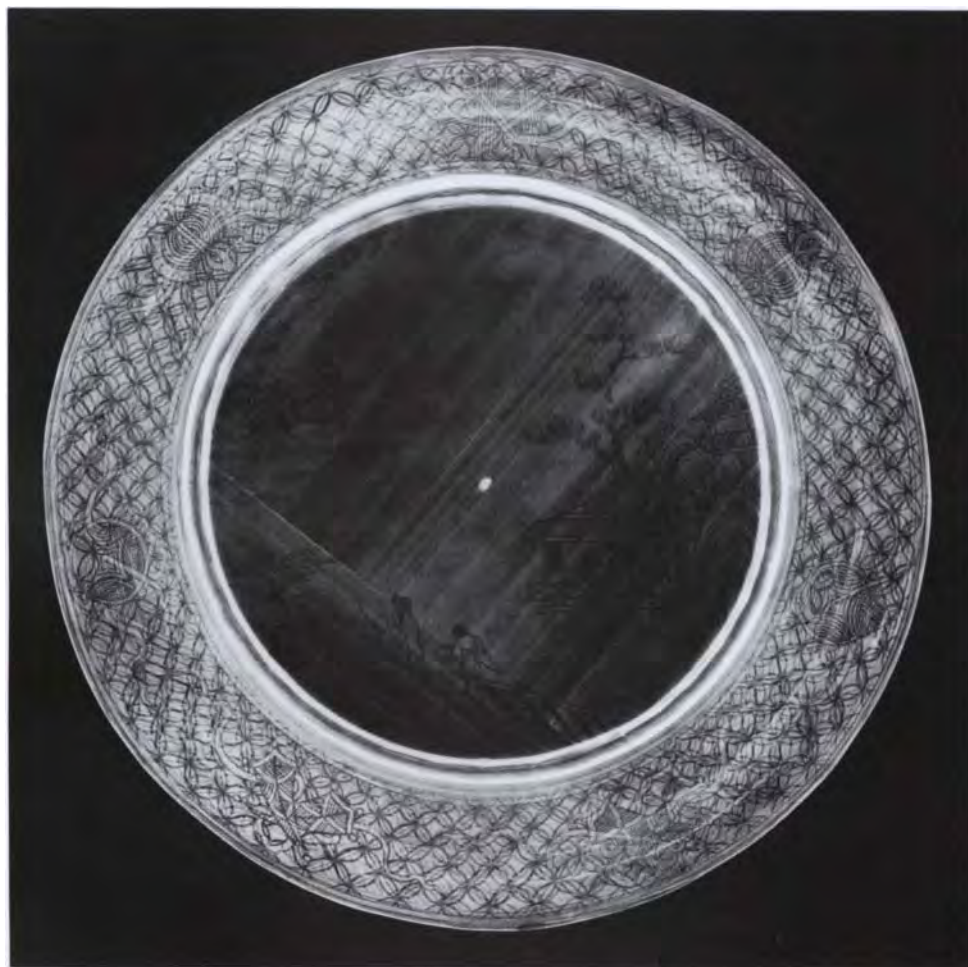


Figure 21. Circular food box with two pheasants and peonies, attributed to Japanese, Muromachi period; height 5.1 cm, diameter 19.0 cm; Los Angeles County Museum of Art M.80.96.1, gift of Dr. and Mrs. Michael Robert Turk.

The decorative motifs are deeply carved into the urushi layers.

Technical data: 45 kV, 5 mA, 1 minute, distance from tube 90 cm. The central areas of the lid and base were fabricated from parallel wood sections. Coiled wood strips form the side. A centering point is visible on both the lid and the base of the box. There are repairs on the foot ring and two floral motifs on the lid.

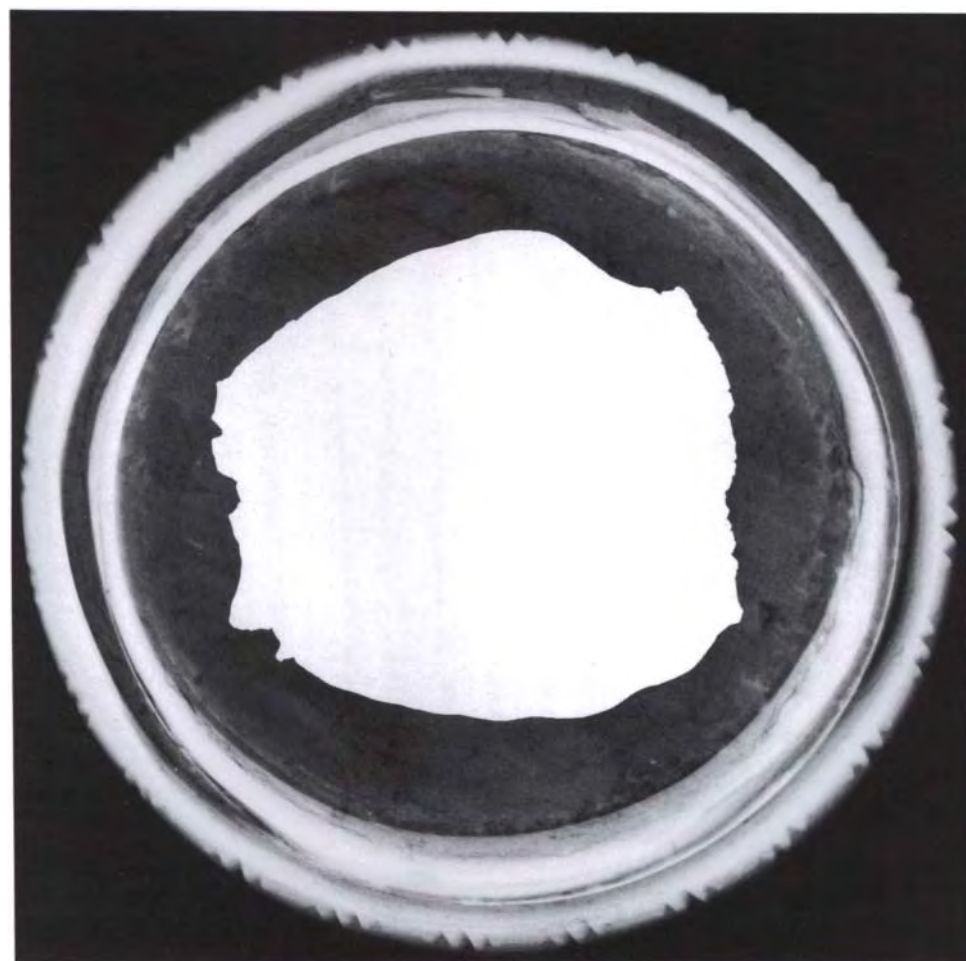
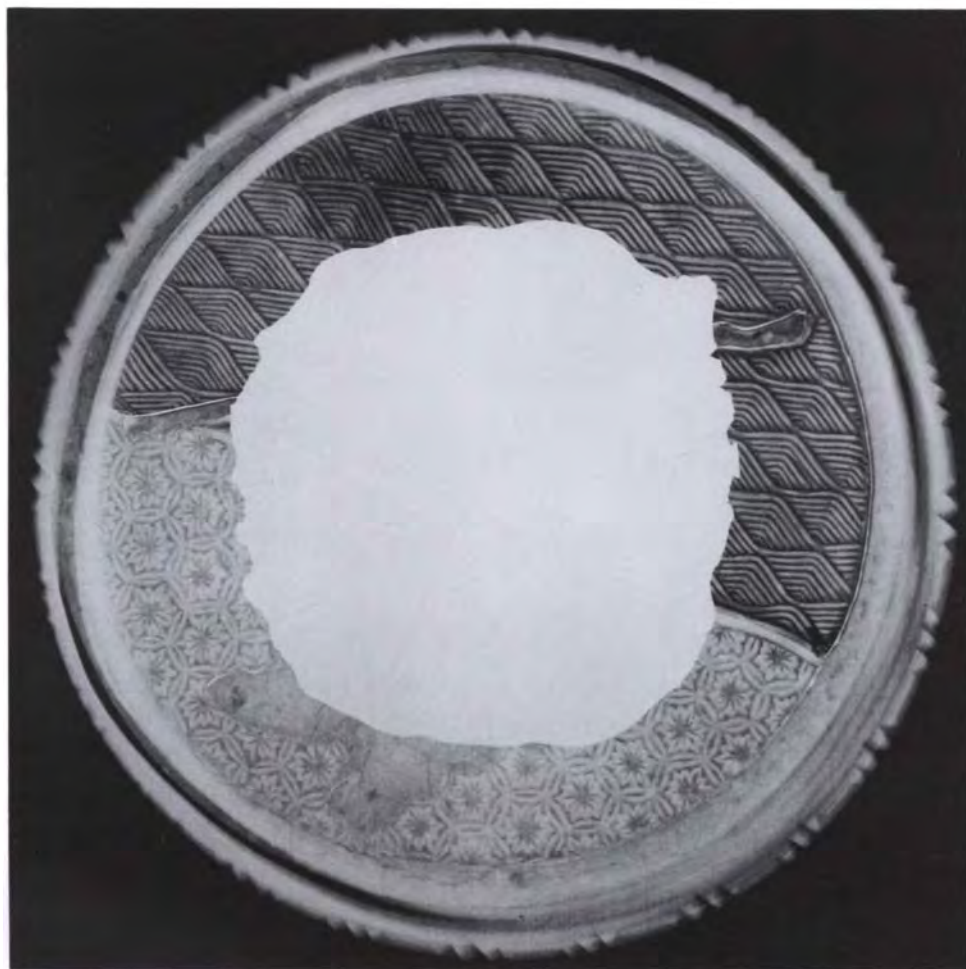
A Chinese example of a similar substructure is LACMA L.82.26.9 (collection of Mr H.K. Lee), carved red urushi circular box with peonies and flowers, Ming dynasty.



Figure 22. Incense box, Japanese, Edo period (seventeenth century); height 2.5 cm, width 6.7 cm; Los Angeles County Museum of Art M.79.182.6, gift of Mr. and Mrs. M.E. Wright.

The box is red and black urushi carved in both low and high relief.

Technical data: 45 kV, 5 mA, 2 minutes, distance from tube 90 cm. Both the lid and the base of the box contain a metal disk in the substructure, possibly used for weighting the object and/or as a support.



## **Conclusion**

Compiled in this paper are the structural characteristics found in a sample of Oriental lacquerware substructures. At this point all the questions raised about urushi substructures and their technology cannot be answered, though we are able to note certain differences.

We think that the use of parallel sections of wood with a single perpendicular member, and parallel sections with two perpendicular members, was developed to prevent the object from warping over time. The coiled wood strip construction used to form the sides of urushi lacquerware may have been a means of preventing warpage or simply a method of forming a circular body without a lathe.

The variety of materials and methods used to reinforce the wood substructure are practical and in some cases decorative. Metal used to protect the rim and the foot was also a decorative element. The use of reinforcing materials such as fabric could be the result of the technological advance to thinner wood substructures, creating a need to give added strength to the delicate wood support. Fabric could also have been introduced to prime or give tooth to the wood substructure for the subsequent layers of urushi.

Several questions still need to be answered. We do not know the purpose of the score lines in the central section of the wood substructure, nor do we know how urushi technology developed, nor how the technology migrated from one culture to another. The examination of urushi substructures by means of radiography gives information that, when collated, will aid the art historian, the conservator and the conservation scientist. By compiling a large body of urushi radiographs, art historians will perhaps be able to determine the provenance of pieces of doubtful origin. Knowing both the surface and the substructural characteristics of Oriental lacquerware, improvements can be made in the conservation, storage, environment and special packing and handling requirements. X-ray radiography will prove invaluable when used in a comparative manner and in conjunction with other analytical and historical data.

## **Acknowledgments**

The information compiled in this paper would not have been possible without the participation of the following individuals and institutions: for x-ray radiography Hélène Gillette, Don Menveg and Dr. Pieter Meyers of the Los Angeles County Museum of Art; Richard L. Barden and Alexis Pencovic of the Asian Art Museum of San Francisco, The Avery Brundage Collection; Dr. Gary Carriveau of the National Gallery of Art, Washington, D.C.; and the Freer Gallery Technical Laboratory, courtesy of the Freer Gallery of Art, Smithsonian Institution, Washington, D.C. For photography, I would like to thank John Gebhardt of the Los Angeles County Museum of Art, and Thomas Moon of the J. Paul Getty Museum (Selections from Freer Gallery, Los Angeles County Museum of Art, and Asian Art Museum of San Francisco); for stereo x-ray radiography, the Freer Gallery, the Smithsonian Institution, Washington, D.C.

In addition, we are indebted to the following persons for the information which came out of numerous discussions: Dr. Pieter Meyers of the Los Angeles County Museum of Art; W. Thomas Chase, Dr. John Winter, and Paul Jett of the Freer Gallery of Art, Smithsonian Institution, Washington, D.C.; Dr. Gary Carriveau of the National Gallery of Art in Washington, D.C.; Suzanne Mitchell of the Detroit Institute of Arts; and Mr Toshikatsu Nakasato of the Tokyo National Research Institute of Cultural Properties.



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# FTIR Analysis of Authentic and Simulated Black Lacquer Finishes on Eighteenth Century Furniture

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The Getty Conservation Institute

## Background

In eighteenth century Europe, Oriental lacquer was a popular furniture finish. This popularity, combined with the scarcity and expense of lacquerware, resulted in the manufacture of furniture with imitation lacquer finishes. Some furniture pieces were made with imported urushi panels mounted on carcasses painted with imitation urushi finishes. These black or red simulated urushi finishes were typically made with natural pigmented resins that lacked the durability of genuine urushi. Today, determination of whether or not a finish is urushi is often based on historical records, appearance (*craquelure*), and solubility tests. Alternatively, instrument analysis may determine the chemical composition and identity of the finishes. In addition to answering the basic question of whether or not the material is urushi, compositional analysis can provide supplementary information for the conservation of the object and on its historical treatment, or past restorations.

Previous researchers have examined the components of urushi by several methods. Burmester (1982) used pyrolysis mass spectrometry (PMS) as a method for the identification of restored areas and forgeries and for the relative dating of East Asian lacquerware. This technique required 300 g of unrecoverable sample as well as complex data handling methods.

Infrared analysis has been used to provide a unique spectral pattern of organic and inorganic functional groups present in urushi compounds. Urushi, a complex mixture of materials, produces overlapping infrared bands which may be difficult to decipher. Kenjo (1977) and Kumanotani (1976) made studies on the changes that occur in the infrared absorption bands during the urushi drying process. From their results it is apparent that the complexity of the urushi matrix increases as the material hardens. This subsequently obscures many of the infrared absorption bands that were distinct in the liquid. However, the remaining pattern of band positions and intensities for cured and aged urushi remains unique. Using a dispersive infrared spectrophotometer, Kenjo (1978) characterized several infrared bands that are significant in the determination of the age and origin of ancient lacquerware.

## **FTIR**

Our studies have been performed on a Fourier Transform Infrared (FTIR) spectrophotometer that has significantly greater spectral sensitivity and resolution when compared to the wavelength dispersive instruments. The design of the FTIR provides high energy throughout, fast scanning speed, and precise wavelength positioning. The computer, required for the complex mathematical calculations, provides the additional benefits of increased signal-to-noise ratio through multiple scan accumulations as well as extensive data storage capabilities. Digitally-stored spectra can be mathematically matched to a large reference library, based upon band intensity and position. These advantages of FTIR over dispersive IR allow smaller samples to be analyzed and bands otherwise difficult to detect to be elucidated.

### ***Microanalytical techniques***

To retain the integrity of an art object, compositional analysis by a non-destructive method is preferred. However, for most organic analysis methods, such as IR, a sample must be taken from the object. In these cases, it is desirable to remove as small a sample as possible, doing as little damage to the object as possible. To analyze these minute samples by FTIR, microanalytical techniques must be applied.

We have taken samples that are barely visible to the naked eye and prepared them for analysis using two microanalytical methods. These methods use beam condensers to focus a high energy infrared beam onto millimeter-size areas. The standard method of IR microanalysis uses a few micrograms of sample diluted with anhydrous KBr and pressed into a transparent pellet. The high pressure diamond cell is another micro-IR method that has been applied successfully to microgram samples from art objects by McCawley (1975) and Laver and Williams (1978). With a diamond cell, any material that flows under pressure may be placed between two diamonds and pressed into a film. This requires minimal sample preparation, and the sample is easily recoverable for further analyses. There will be no side-effects due to sample interaction with the KBr or to the hygroscopic tendencies of the KBr.

There are inherent problems when sample size is restricted and microanalytical methods are applied. Homogeneity of the material at the microscopic level is critical if the sample is to be representative of the object. At the microgram level any source of contamination, even a dust speck, can significantly bias the results. Careful sample selection, handling, and preparation procedures can reduce these problems. As the sample size increases, the relative consequence of micro-variations decreases. These considerations must be weighed against the amount of sample that may be taken from an object.

### ***Objective***

The objective in this study was to apply both the high resolution and good sensitivity of FTIR and the minimal sampling requirements of microanalytical methods to the analysis of finishes on oriental-style furniture. The primary question was whether the furniture finishes were urushi or imitation. IR analysis proved successful for the identification of these finishes.

### ***Experimental***

IR spectra were obtained at  $4\text{ cm}^{-1}$  resolution on a Digilab 15-E FTIR spectrophotometer equipped with a Motorola 3200 computer and a dry nitrogen gas purge. A wide-range, cryogenically cooled mercury-cadmium-telluride (MCT) detector was used for the examination of the mid-IR range from  $4000\text{-}500\text{ cm}^{-1}$  ( $2.5\text{-}20\text{ }\mu\text{m}$ ).

### *KBr micropellet*

Microgram quantities (20–50 µg) of sample were diluted with anhydrous KBr powder, uniformly mixed and pressed under vacuum with a Perkin Elmer die into a 1.5 mm diameter micropellet. This formed a transparent disk which was placed at the focal point of a Harrick Scientific 4x beam condenser for transmissive analysis. An accumulation of two hundred scans was Fourier transformed and ratioed with a background spectrum of nitrogen traversing the same path length. All data were represented as absorbance spectra.

### *Diamond cell*

Microgram quantities (20–50 µg) of sample were placed between two diamonds and pressed with minimal pressure into a transmissive film. The high pressure Diamond Optics diamond cell was then placed at the focal point of a Harrick Scientific 6x beam condenser that was specially modified to accommodate the cell. The beam condenser provides increased energy throughout, which is required since the diamonds only transmit 5–6% of the total beam energy. Diamonds are considered opaque in the region from 1750–2650 cm<sup>-1</sup>. Five hundred scans were co-added, Fourier transformed, and ratioed against a background spectrum obtained from the empty diamond cell. The diamonds were cleaned between samples with methanol and checked with an optical microscope for cleanliness and alignment.

## **Sampling**

Reference samples of aged urushi were obtained from objects of known provenance from the Far East Asian collection of the Los Angeles County Museum of Art. The reference set contained six selections, two each from Japan, China, and Ryukyu, with either red or black pigmentation. The sample set was composed of furniture pieces from the Decorative Arts collection at the J. Paul Getty Museum (Table 1). Several of these pieces are illustrated in the paper by Westmoreland in this volume. Each piece was of eighteenth century European manufacture in the Oriental style with a black lacquerlike finish. Samples were chosen arbitrarily from obscure areas on the furniture, near or under gilt brass mounts. In each case, the area to be sampled was cleaned with solvent to remove any dust or superficial coating. A scalpel was used to remove small, barely visible amounts of the surface layers of the finish. Since only a few samples of minimal size were taken from each object, the assumption had to be made that the selections were representative.

**Table 1. Summary of the sampling and analysis of Oriental lacquer-like finishes on furniture**

<i>Acquisition number</i>	<i>Description of furniture</i>	<i>Sampling area</i>	<i>Finish analysis interpreted from infrared spectra</i>
55.DA.2	French commode c. 1750 set with panels of black Japanese lacquer	1. Right side 2. Front, right side	Urushi Urushi
65.DA.4	French commode c. 1737 set with panels of black Japanese lacquer, surrounding areas painted with <i>vernis Martin</i>	1. Front, left door inside panel 2. Right side, inside panel 3. Right side, under panel	Urushi Urushi Non-Urushi
84.DA.74	Chinese black lacquer plate, bowl, and lid	1. Plate—underneath near lip 2. Bowl—inside near handle 3. Bowl—outside near foot 4. Lid—outside under knob 5. Lid—inside next to rim	Urushi Urushi Urushi Urushi Urushi
83.DA.280	French cartonnier c. 1745 decorated with black <i>vernis Martin</i>	1. Front, left half 2. Top portion, right side in panel	Shellac Shellac
78.DA.119	Pair of corner cupboards, c. 1755. Veneered with panels of Japanese lacquer. Set with gilt-bronze mounts.	6. Right cupboard—left front—under mount—black 7. Right cupboard—left front—under mount—yellow varnish 8. Left cupboard—left front—under mount	Copal or sandarac Copal or sandarac Copal or sandarac
71.DA.104	French secretaire c. 1785, veneered with panels of Japanese lacquer	1. Front center, in panel 2. Bottom shelf, rear inside 3. Front hole under horse's leg	Shellac Shellac Urushi

Figure 1. Infrared absorbance spectra of two urushi samples. The sample on top is from a black lacquered Ryukyun tray, and the sample on bottom is from a panel on a black lacquered commode. This visual identification was concurred by computer matching.

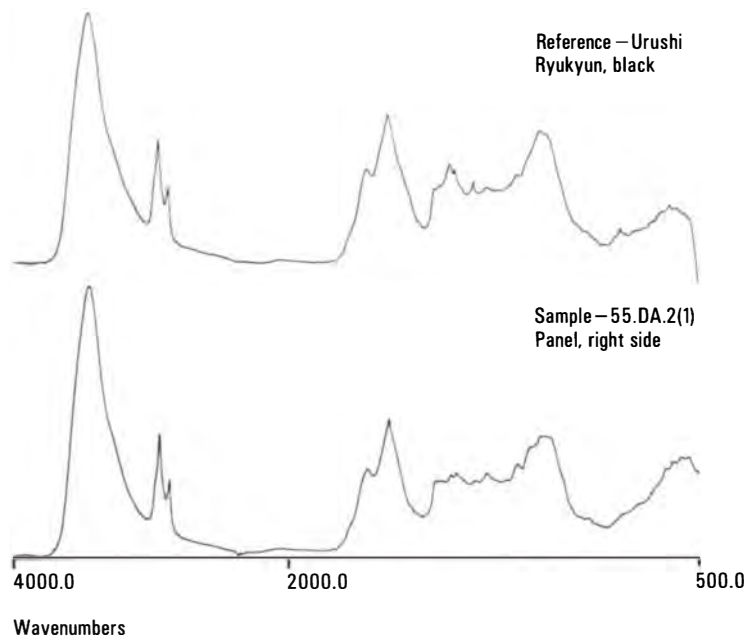
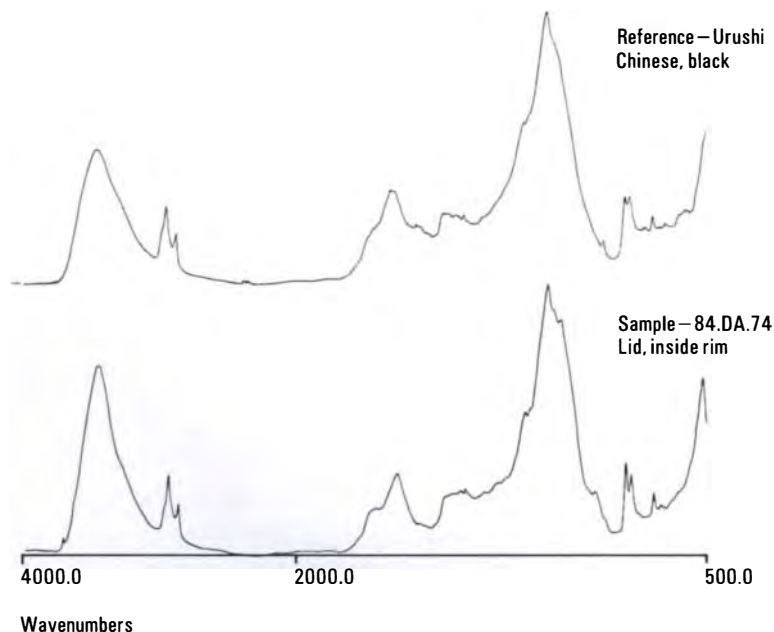


Figure 2. Infrared absorbance spectra of two urushi samples. The sample on top is from a Chinese black lacquered food bowl, and the sample on bottom is from the lid of a black lacquered bowl set thought to be of Japanese origin. This visual identification was concurred by computer matching.



## Results

### Reference spectra

Two distinct patterns were observed in the infrared spectra of the urushi reference sample. Spectra representative of these two variations are shown in Figures 1 and 2. The differences do not preclude the identification of the urushi complex. Bands previously identified by Kenjo (1978) as source-independent are observed in both patterns. These and additional absorbance bands consistently found in our set of reference spectra are listed in Table 2. The reference set contained urushi of differing manufacture, but the limited number of samples prohibited any conclusions regarding the source-dependent spectral variations.

The major difference in the two patterns consisted in relatively large absorbances due to siliceous material (Fig. 2). The strong band at  $1070\text{--}1080\text{ cm}^{-1}$ , along with the absorbances at  $796$  and  $779\text{ cm}^{-1}$ , are due to quartz. Additional absorbances at  $1030$ ,  $3620$  and  $3698\text{ cm}^{-1}$  are due to clay. Garner (1963) indicated that the silicon portion of the lacquer in his samples was due to contamination from the ground layer. However, no ground layer was present in these samples. This seems to indicate that the silicon material may have been an additive in the manufacturing process.

Neither the red nor the black lacquer samples in the reference set produced differentiable infrared bands that could be attributed to the pigmentation. This corresponds to Garner's (1963) determination that pigments typically used to color lacquer are vermilion and carbonaceous material for red and black, respectively. These colorants do not produce significant infrared bands in the spectral region examined.

**Table 2. Characteristic absorption bands observed in Oriental lacquer**

<i>Source-Independent</i>		<i>Source-Dependent</i>
<i>Kenjo (cm<sup>-1</sup>)</i>	<i>This study (cm<sup>-1</sup>)</i>	<i>Kenjo (cm<sup>-1</sup>)</i>
3400	3450	1595–1720
2925	2926	993
2850	2885	
1430–1465	1435–1465	
1065	1315	
	1145–1165	
	1050–1090	

### Sample Spectra

Interpretations of the spectral features of the samples from the oriental-style eighteenth century European furniture are given in Table 1. The characteristic band positions and intensities were taken into consideration in the comparison of the sample spectra with the reference urushi and natural resin spectra. In addition to the visual comparison, computer matching was done. A reference library of spectra, which included the six urushi samples and other natural resins, was searched for the best fit to the unknown spectra. The computer matches corresponded to the visual identifications. The matches and their hit values, based on peak position and intensity, are given in Table 3.

Urushi-based resin finishes were found on several pieces. Panels from the French commode, 55.DA.2, have an urushi finish as illustrated by the spectra in Figure 1. Samples from a plate, bowl, and lid, 84.DA.74, were verified as urushi, as illustrated by the spectra in Figure 2. Slight spectral differences found between the pieces in the set may indicate that the bowl has a different source of manufacture from the lid and plate. As seen in Table 3, the computer matched the bowl with the Japanese urushi reference, while matching the lid and plate with the Chinese urushi reference. This is a tentative assignment that may be confirmed by comparison with

**Table 3. Results of comparison of finish samples with spectra library**

<i>Acquisition number</i>	<i>Description of furniture</i>	<i>Sampling area</i>	<i>Hit quality index*</i>	<i>Computer match reference material</i>
55.DA.2	French commode c. 1750 set with panels of black Japanese lacquer	1. Right side	0.07	Urushi, Ryukyu, black
		2. Front, right side	0.07	
65.DA.4	French commode c. 1737 set with panels of black Japanese lacquer, surrounding areas painted with <i>vernis Martin</i>	1. Front, left door inside panel	0.06	Urushi, Ryukyu, black
		2. Right side, inside panel	0.10	
		3. Right side, under panel	0.10	
84.DA.74	Chinese black lacquer plate, bowl, and lid	1. Plate—underneath near lip	0.07	Urushi, China, black
		2. Bowl—inside near handle	0.06	
		3. Bowl—outside near foot	0.08	
		4. Lid—outside under knob	0.03	
		5. Lid—inside next to rim	0.04	
83.DA.280	French cartonnier c. 1745 decorated with black <i>vernis Martin</i>	1. Front, left half	0.10	Shellac
		2. Top portion, right side in panel	0.07	
78.DA.119	Pair of corner cupboards, c. 1755. Veneered with panels of Japanese lacquer. Set with gilt-bronze mounts.	6. Right cupboard—left front—under mount—black	0.13	Copal
		7. Right cupboard—left front—under mount—yellow varnish	0.07	
		8. Left cupboard—left front—under mount	0.10	
71.DA.104	French secretaire c. 1785, veneered with panels of Japanese lacquer	1. Front center, in panel	0.09	Shellac
		2. Bottom shelf, rear inside	0.08	
		3. Front hole under horse's leg	0.06	

\*The hit quality index is a measure of the difference between the unknown spectra and the library spectra. A HQI of 0.0 indicates that there is no difference and higher HQIs indicate an increasing amount of dissimilarity. A HQI below 0.15 indicates nearly identical spectra (Sadler 1985).

Figure 3. Infrared absorbance spectra of two shellac varnishes. The sample on top is shellac resin, and the sample on bottom is from the surface of a black lacquer-like secretaire. Another sample from below the surface was urushi.

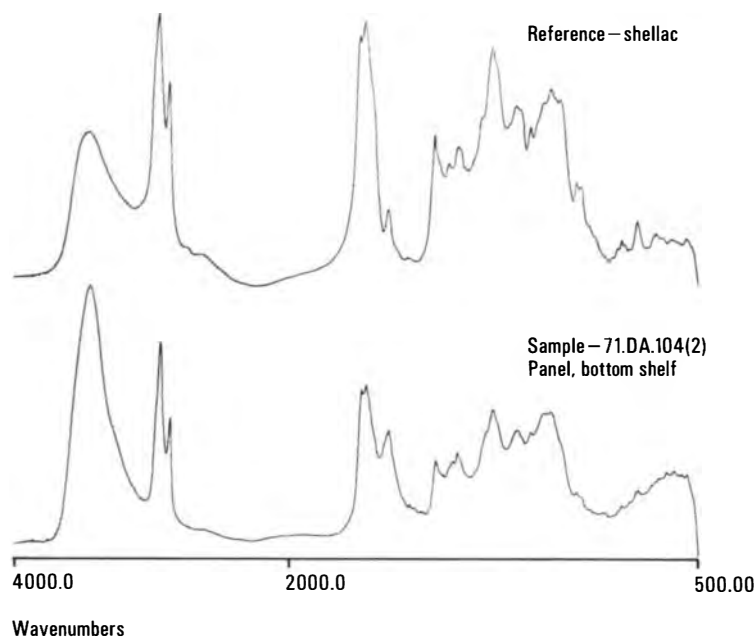
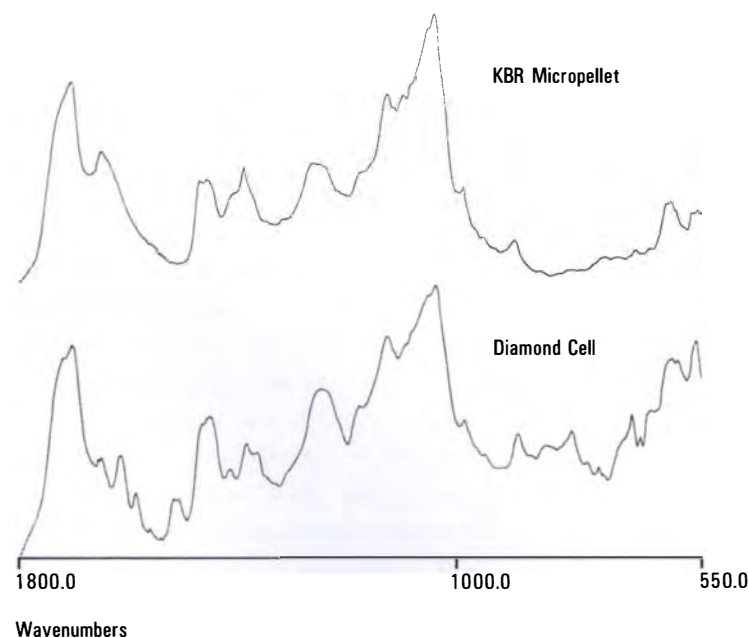


Figure 4. Two infrared absorbance spectra of the finish on the right corner cupboard, 78.DA.119. For the spectrum on top, the sample was prepared as a KBr micropellet, while the spectrum on bottom was analyzed using a diamond cell.



a larger reference base. Since we analyzed only two pieces for each manufacturing source (Japan, China, and Ryukyu) as references, it is not clear whether variations similar to those seen between pieces made in different countries may occur between pieces manufactured within one country.

Some European furniture pieces consisted of custom-made frames for imported Oriental lacquer panels. An example of this is the French commode labeled 65.DA.4. Samples taken from two of its panels were found to be urushi. However, the sample taken from below the panel on the right side of the commode is not urushi, indicating that the framework is painted with a pigmented varnish.

In a third group of pieces, pigmented natural resin finishes were found on the inset panels. The varnish on the French cartonnier, 83.DA.280, is shellac-based, while the varnish on the pair of cupboards, 78.DA.119, is copal or sandarac. This is consistent with the cracked appearance of the finish on these pieces.



The results for the finishes described above corresponded to the curatorial information provided. However, the finish on the French secretaire, 71.DA.104, was inconsistent with the expected results. As shown in Table 1 and Figure 3, samples from the front center section and the center panel on the bottom shelf are shellac. Since the piece was expected to be urushi, another sample was taken from a nick in the bottom shelf. This third sample was found to be urushi, which suggests that the piece was originally urushi but had been coated with shellac. One must be cautious in assuming that microgram quantities of material are representative of the entire piece when interpreting analytical results.

### **Microanalytical Methods**

Each of the samples was analyzed by both KBr micropellets and a diamond cell. The spectra obtained from both techniques are similar (Fig. 4). Slight spectral deviations are attributable to the different methods.

KBr is hygroscopic and easily absorbs trace amounts of organic compounds from the atmosphere. When very small amounts of sample, i.e., 10  $\mu\text{g}$ , are mixed with KBr, any contamination in the KBr is more apparent in proportion to the intensity of the sample absorption bands. Hence, the hydroxy bands ( $3450, 1630\text{ cm}^{-1}$ ) and the C–H bonding vibrations ( $1400, 1384\text{ cm}^{-1}$ ) are more prevalent in the spectra from KBr micropellets than in the corresponding spectra obtained from the diamond cell. Nonetheless, the spectra obtained by KBr micropellet are reproducible and are directly comparable to most published and digitally stored reference spectra.

The diamond cell eliminates the effects of water absorption or sample interaction due to the presence of KBr, and the sample is readily recoverable. However, there is an artificial enhancement of the absorbance bands at lower wave numbers, and diamonds do not transmit the infrared beam from  $2650\text{--}1750\text{ cm}^{-1}$ . Because of the opaque region and this apparent amplification at low wavenumbers, agreement with reference spectra may not be obvious. Band position information is more reliable than band intensity information obtained from the diamond cell spectra. This limits the usefulness of computer matching techniques which rely on both sources for comparison. Although the two microanalytical techniques, KBr micropellet and diamond cell, are not equivalent, they are comparable and provide complementary information. Each method has its advantages and either may be used for the identification of the microgram quantities of resin analyzed in this study.

### **Conclusion**

This study demonstrates that FTIR can be used to identify urushi versus pigmented natural resins for the characterization of oriental-style European furniture. Microgram quantities of sample, barely visible to the naked eye, were removed from each piece for spectral analysis. The samples were found to fall into three categories: urushi-based resin finish on the entire piece; urushi-based resin on inset panels only; resin other than urushi.

Microanalytical FTIR techniques were used to classify the samples in these categories, based on a reference set of samples of known origin. Attributions to country of origin were not made in this study because of the limited size of the reference set. However, when more pieces of known manufacture have been analyzed to provide a statistically sound reference base, attributions may be possible.

As in any microanalytical technique, caution must be exercised when extrapolating the results of a small sample. This consideration must be weighed against the amount of sample which it is desirable to take from a valuable object. When only limited samples may be taken, the two IR microanalytical techniques, micropellets and diamond cell, may be used for accurate characterization of the sample.

## **Acknowledgment**

We would like to thank George Kuwayama, curator of Far Eastern Art at the Los Angeles County Museum of Art, for generously allowing us to obtain Oriental lacquer samples from artifacts of known provenance and age for our reference spectra.

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# Solvent Testing Method for Identification of Oriental Lacquer Used in European Furniture

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The collection of the J. Paul Getty Museum in Malibu, California, contains eleven pieces of furniture made in Paris between 1735 and 1785 that incorporate lacquer panels surrounded by *vernis Martin* or veneers and decorated with gilt bronze mounts. Of these eleven pieces, nine are stamped with the name or initials of the *ebeniste*, but these marks provide no information about the creator of the lacquerwork.

It was a practice throughout Europe to employ both Far Eastern lacquer and European imitations in the manufacture of furniture and other objects. Today, this presents problems of identification and classification for museum curators and others. This paper describes an experimental method of using solvents to distinguish between Oriental and European lacquer. The solvent testing was followed by sampling and technical analysis at the Getty Conservation Institute (see Derrick, Druzik, and Preusser, this volume). The results were identical, with a single exception which will be described.

These methods may not be the ultimate answer to the problem of accurately identifying each section of a large piece when modifications, restorations, or other changes have taken place. However, when a museum has no access to analytical facilities or when funds for such investigations are limited, the solvent method may be of use.

## ***Seventeenth and eighteenth century European lacquerware***

When the Dutch and British East India companies began importing Asian lacquerware, they created a fashion that was to extend throughout Europe and colonial America. To meet the increasing demand, the Dutch East India Company provided the specifications for various objects, especially cabinets and chests, and had the pieces made in the Far East (Jarry 1981:128). In 1670, English craftsmen were sent to China to teach Chinese artisans how to make objects that would be suitable for sale in Western markets. This practice soon created a threat to the domestic industry, and in England at the beginning of the eighteenth century the master craftsmen complained of the volume of Oriental lacquerware being imported (Jarry 1981:132). John Stalker and George Parker published in 1688 their *Treatise of Japanning and Varnishing*, a booklet of recipes and instructions for varnishing and lacquering in the Oriental style. Thus it was a relatively simple matter for craftsmen in the West to develop their own methods and materials for obtaining the desirable appearance of lacquer. In England and America the term "japanning" came to mean a style of furniture decoration that employed a painted black background with shallow relief ornamentation made

with gesso, gilded or painted with metal powder, and finally coated with several coats of varnish to simulate the brilliance of lacquer.

In Italy in 1690, Cosimo III de' Medici commissioned a scientific study of the resin used in the fabrication of Chinese lacquer; however, the only result was that the investigator became ill (Jarry 1981:134). In 1720 the Jesuit Filippo Bonanni published *Trattato sopra la vernice*. He used the studies in Florence between 1690 and 1700 as the basis of a thorough and authoritative account of the origins of the raw material of Chinese lacquer, as well as the difficulties of handling the raw lacquer and its toxic potential. He drew the conclusion that Europeans "should content themselves with substitutes, since Chinese resin would not tolerate transfer from the Far East to Europe and since the tree called Tri would not grow in a Western climate" (Jarry 1981:134).

Bonanni's treatise was translated into French in 1723. By this time lacquered furniture was quite the rage, although the type of piece (commode, secretaire, carton-nier, etc.) had nothing to do with the Orient. The terms applied to these pieces were imprecise: *verniss de la Chine*, *verniss de lacque*, *lacq ancien*, and *verniss Martin*. By 1730 it was fashionable to mount Chinese or Japanese lacquer panels directly on the furniture like inlay or pieces of veneer, and certain cabinetmakers specialized in making carcasses to which the lacquer could be attached. Frequently the Oriental lacquer was retouched by a Parisian cabinetmaker in order to make the piece appear as a unified whole. Practices such as this can make it extremely difficult to distinguish imported Asian lacquer from the domestic European kind.

In the middle of the eighteenth century, there was an atelier of extraordinarily skilled craftsmen, the Martin family, who worked through two generations. Much of their work was for the royal court at Versailles. They had numerous imitators and pieces can generally only be attributed to them on account of the excellence of the craftsmanship, since no signed piece exists. Their method of finishing required the surface to be prepared with forty-three layers of chalk white. Five layers of paint were then applied, followed by fifteen layers of varnish (Huth 1971:96). In 1753, the two oldest brothers were granted a royal patent for the invention of a lacquer with a copal resin base. The dissolving of the hard copal resin in alcohol created a thick, hard, dark varnish, and was probably the *verniss Martin* for which they became world renowned (Huth 1971:95). The Martins are also known to have made repairs on Oriental lacquer; the repair of lacquer was an important part of their craft.

Therefore, use of "lacquered" to describe furniture from this period is often no more than a general description of a decorative style. The tests described here may help to identify the technique and materials used. It should be noted that an experienced curator specializing in this field can generally distinguish between European and Oriental material by stylistic judgment. An experienced conservator can also make judgments based on deterioration of the object, as for example when cleavage reveals lower layers.

### **Tests with solvents**

Solvent testing should be carried out where there is good access to the questionable areas. For example, removal of a door may facilitate the removal of a mount, permitting inconspicuous testing. As the tests proceed, strong lighting will make it easier to see areas of overpainting on the dark surfaces. These areas can be eliminated at the outset if there are other areas that seem to have fewer layers to be penetrated.

The location of tests should be precisely recorded. If samples are to be taken later for analysis, the test area will already be clean. Test areas should be original panels and not locations that may have had alterations, such as a door with a lock-plate; these later additions or modifications may have been painted to match the original lacquer. The test spot should be located either under a removable mount or

in a part of the design where it will be unnoticed. It is also advisable to have all possible treatment records at hand, as certain types of coating material applied in a past restoration may be insoluble and thus cause uncertainties.

The selection of solvents is based on the solubility of various films and coatings in organic solvents (Gettens and Stout 1966:204–205). The uppermost layers may be furniture wax or polish, and these can be removed with turpentine or xylene, using a small cotton swab and cleaning an area approximately 1 cm<sup>2</sup> or smaller.

Other modern finishes used by restorers may be insoluble in the above solvents and reagents and an expanded range of solvents and solvent mixtures may be required. Urushi appears to be soluble only in nitric acid. Paint strippers based on methylene chloride (dichloromethane) can be tried.

**Table 1. Coatings and solvents**

<i>Surface coatings</i>		<i>Solvents and reagents</i>
Natural resins	Dammar	Acetone
	Mastic	Acetone, diacetone alcohol
	Sandarac	Acetone, diacetone alcohol
	Copal	Acetone, ethanol, diacetone alcohol, Cellosolve® (2-ethoxyethanol)
	Shellac, seed-lac	Ethanol, diacetone alcohol
Waxes		Turpentine, xylene, toluene
Synthetic resins	Polyvinyl acetate	Xylene, toluene, ethanol
	Acrylic polymer (Paraloid®)	Xylene, toluene
Dried linseed oil		Ethanol, morpholine, dimethylformamide



Figure 1. *Commode* (a), attributed to Joseph Baumhauer, French, c.1750; Darnault label underneath (b). Oak veneered with black lacquer panels, gilt bronze mounts. J. Paul Getty Museum, 55.DA.2.

Test area no. 1: top drawer, front, under mount, proper left end. Acetone removed varnish and black overpaint and revealed a hard, brown, insoluble surface. Ethanol produced the same results.

Test area no. 2: proper left side, bottom center of panel. Acetone removed varnish and black overpaint and revealed a hard, black, insoluble surface. Ethanol produced the same results.

We concluded that these were urushi panels with additional European surface coatings or overpaint.



Figure 2. Commode (a) by Bernard van Risenburgh, French, c.1737. Veneered with Japanese black lacquer and vernis Martin, gilt bronze mounts. J. Paul Getty Museum, 65.DA.4.

Test area no. 1: keyhole, front, proper left door (b). Acetone removed yellow varnish. Ethanol removed varnish and black paint, exposing white gesso.

Test area no. 2: front, proper left door, bottom of panel (b). Acetone removed yellow varnish and black paint and revealed a black insoluble surface. Ethanol produced the same results.

Test area no. 3: proper left side, bottom left corner (c). Acetone removed varnish and revealed a hard, black, insoluble surface. Test area no. 4: proper left side, center (c). Acetone removed varnish and revealed a hard, black, insoluble surface.

We concluded that this was urushi with additional European surface coating and overpaint.



Figure 3. *Secrétaire*, attributed to Jean-Henri Riesener, French, c.1785. Veneered with Japanese lacquer and ebony, gilt bronze mounts. J. Paul Getty Museum, 71.DA.104.

Test area no. 1: front, lower left side, immediately adjacent to central mount; the mount was difficult to remove and removal might have caused damage. No surface coatings were removed with xylene, acetone or ethanol.

Test area no. 2: circular panel on bottom shelf, proper right top corner. No surface coatings were removed with xylene, acetone or ethanol.

At this stage, test area no. 2 was sampled. The results showed a shellac-based material, giving a contradictory result to the solvent test. The test area was slightly enlarged and the surface was cleaned with dimethylformamide. No residue was visible on the swab. A further sample was taken for analysis, the results of which showed the coating to be urushi. This piece was restored in 1973 on a contract basis for the J. Paul Getty Museum and no treatment report is on file. A modern surface coating may have been used, which might account for the discrepancy in the initial result. This experience indicates that caution should be exercised when interpreting solvent tests.

We concluded that this was urushi with additional European surface coatings and overpaint.



Figure 4. *Cartonnier and serre papier* by Bernard van Risenburgh, French, c.1745–49. Oak veneered with vernis Martin, enameled and painted metal, gilt bronze mounts. J. Paul Getty Museum, 83.DA.280.

Test area no. 1: front, proper right side of lower panel. Acetone very slowly removed yellow varnish. Ethanol removed black paint, exposing white ground.

Test area no. 2: proper left side of *serre papier*. Acetone very slowly removed yellow varnish. Ethanol removed black paint, exposing white ground.

We concluded that this was a European shellac-based coating.





Figure 5. Pair of corner cupboard by Jacques Dubois, French, c.1755. Oak veneered with vernis Martin and set with lacquer panels, gilt bronze mounts. J. Paul Getty Museum, 78.DA.119 a and b.

Test area no. 1 (a): proper right side of door, under upper mount. Acetone removed yellow varnish followed by black paint. Ethanol quickly removed black paint. Beneath this there was no sign of gesso but, as paint was removed, fine horizontal cracking remained and the area continued to be tacky. Visual examination revealed much prior loss and overpaint.

Test area no. 2 (b): between front legs of proper left-hand horse. The results were the same as for test area no. 1.

We concluded that further testing should be done on this piece. X-radiographs might show other decorated layers beneath the present surface, which is a European coating of shellac or some other resin.



## **Acknowledgments**

I would like to thank the J. Paul Getty Museum for the opportunity to investigate pieces in the collection, Gillian Wilson for her support of the project, Diane Biehl for preparing the transcript, and Barbara Roberts for assisting with solvent testing and the final preparation of the paper. The analytical work (see Fig. 3) was carried out by Michele Derrick.

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# The Chemistry of Oriental Lacquer (*Rhus Verniciflua*)

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The art or technique of lacquerware came to Japan from China via Korea with Buddhism in the sixth century. Since then, it has been modified and developed in response to the characteristics of the culture of each period as well as to local natural features, such as weather and products such as clay, wood, etc.

Lacquerware techniques cannot be understood without a knowledge of the chemistry of sap and lacquer as materials, especially in the preservation and restoration of cultural properties.

## Properties of lacquer

When compared with synthetic coatings, the most prominent property of Oriental lacquer is its excellent durability, which has been demonstrated by the use of lacquerware since ancient times. In Japan and China, and in some museums in the United States and Europe, there are large numbers of Japanese lacquer objects that have been preserved for thousands of years or excavated in their original condition.

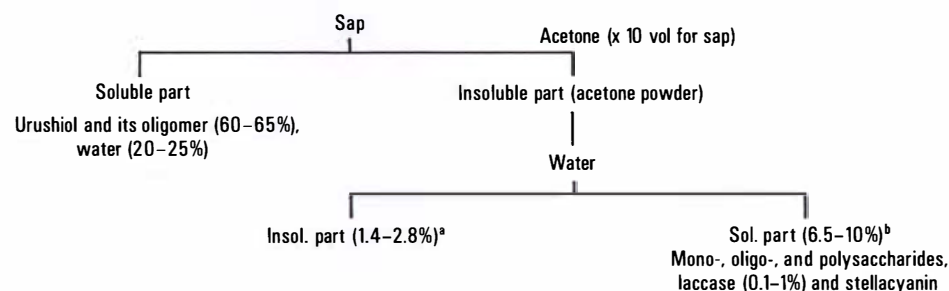
Lacquer layers exposed to open air degrade to a powdery efflorescence without losing the beauty of their appearance.

Lacquer is adhesive and electrically insulating, and it is sometimes used as a structural material. Moreover, lacquerware is beautiful, smooth to the touch, and yet, solid. These characteristics are unique to this material.

## Constituents of the sap of the lacquer tree, *Rhus verniciflua*

The sap of the lacquer tree is a water-in-oil emulsion. Analysis of the sap constituents, carried out by the application of gel permeation chromatography (GPC) and high performance liquid chromatography (HPLC) in combination with the Japanese Institute of Standards method K5950, is shown in Table 1.

Table 1. Analysis of sap constituents



<sup>a</sup>Nitrogenous substances and <sup>b</sup>gummy substances in JIS K5950

Figure 1. Urushiol isomers in sap (*Rhus verniciflua*).

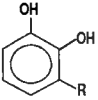
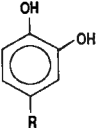
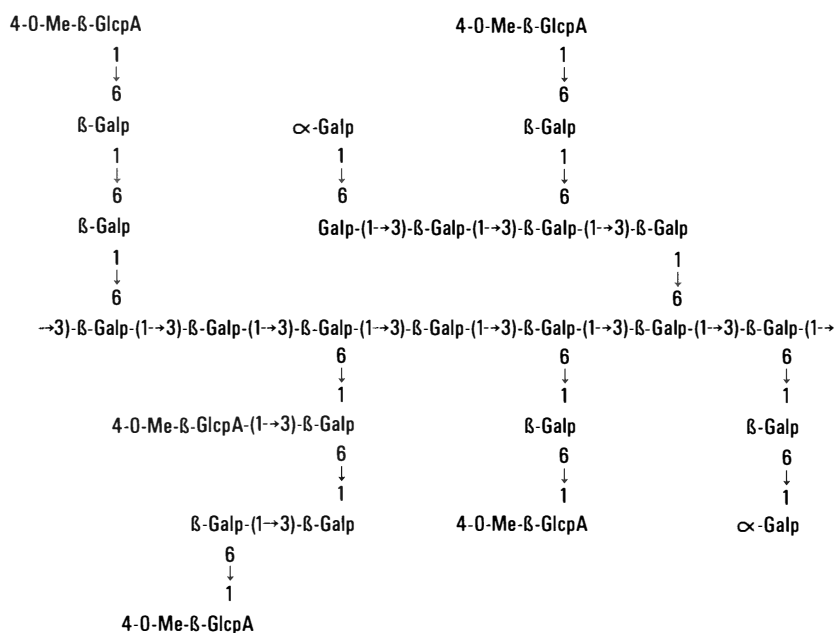
	R	%	
	1	15:3 8'cll't13'c	67.0
	2	15:3 8'cll'c14'e	0.1
	3	15:3 8'cll't13't	0.3
	4	15:2 8'cll'c	2.5
	5	15:2 8'cll't	1.2
	6	15:1 8'c	20.6
	7	15:0	3.6
	8	17:3 10'c13't15'c	0.4
	9	17:3 10'c13'c16'e	0.1
	10	17:2 10'c13'c	0.4
	11	17:1 10'c	0.1
	12	15:3 8'cll't13'c	3.0
	13	15:3 8'cll'c14'e	0.1

Figure 2. Structural features of acid from polysaccharides.



Urushiol, the major component of the sap, is a mixture of 3-substituted pyrocatechol derivatives with a saturated or unsaturated chain of fifteen (major) or seven (minor) carbon atoms as shown in Figure 1 (Du 1984:463).

Nitrogenous substances, isolated as a water-insoluble part of the acetone powder (see Table 1), are insoluble in most organic solvents, but dispersible or dissolved in urushiol as a stabilizer of the water droplets in the native sap, because the original sap emulsion cannot be made without these nitrogenous substances (Kumanotani 1985:163). The <sup>13</sup>C/MAS spectrum, IR spectrum and chemical analysis lead to the conclusion that the nitrogenous substances are glycoproteins (sugar/protein = 1/9 w/w). They become soluble in SDS-water when reduced with 2-mercaptoethanol, and were found to be giant molecules linked with S-S bonds between the fragments, with molecular weights of 8,000 and 17,000 (major) and 25,000 and 47,000 (minor).

Gummy substances are mainly dissolved in the water droplets in the sap and are composed of mono-, oligo-, and polysaccharides (Oshima 1984:43). The polysaccharide was separated by aqueous-phase GPC into two fractions having molecular weights 84,000 and 27,000. The fractions contain D-galactose (65 mol%), 4-O-methyl-D-glucuronic acid (24 mol%), D-glucuronic acid (3 mol%), L-arabinose (4 mol%) and L-rhamnose (3 mol%). Smith degradation of the carboxyl-reduced polysaccharides

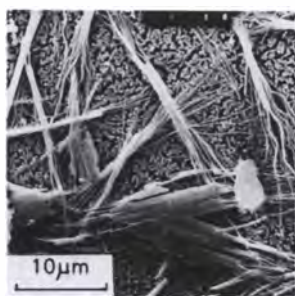


Figure 3. SEM photomicrograph of the fibrous polysaccharides.

gives products of halved molecular weight, and these consist of a  $\beta$ -(1-3)-linked galactopyranan main chain and side-chains made up of galactopyranose residues. Peripheral groups, such as  $\alpha$ -D-Galp-,  $\alpha$ -D-Galp-(1 $\rightarrow$ 6)- $\beta$ -D-Galp-, 4-O-methyl- $\beta$ -D-GlcpA- and 4-O-methyl- $\beta$ -D-GlcpA-(1 $\rightarrow$ 6)- $\beta$ -D-Galp-, are attached to this interior core through  $\beta$ -(1 $\rightarrow$ 3)- or  $\beta$ -(1 $\rightarrow$ 6)- linkages as shown in Figure 2.

Despite the branched structure, the polysaccharides are able to make a fibrous network (see Fig. 3) that participates in producing durable lacquer films, as will be explained later.

Laccase is a copper glycoprotein, p-quinol-O<sub>2</sub>-oxidoreductase with  $M_n$  of 120,000 and four atoms of copper per molecule, consisting of common amino acids (55%) and sugars (45%), indicating a reduction potential 415 mV at 25°C and pH 7.4 (hydroquinone as substrate) respectively (Nakamura 1958:538). Stellacyanin is also a copper glycoprotein with  $M_n$  of 20,000, which shows a low reduction potential (184 mV, pH 7.0; Lappin 1981:34). Its role in the sap or lacquer is not yet known. Laccase and stellacyanin are likely to be distributed in both the water droplets and the urushiol phase of the sap.

### **Durability of Oriental lacquer films**

From measurements of the dynamical property of sap and lacquer films by the torsional pendulum method, it has been demonstrated that sap films undergo a large degree of chemical cross-linking over a period of three years, but the lacquer film keeps almost the same degree of cross-linking (Kuwata 1961:1678). Recently the same conclusion was extended to lacquer and sap films stored over twenty years, from the measured dynamical property of the same films (Kumanotani 1981:643; 1983:225). Variation of density is shown in Table 2 for sap and lacquer films stored for nineteen years. This indicates almost no variation of density for lacquer films, but a remarkable change for sap films. These results demonstrate that the lacquer is substantially different from the sap. The lacquer gives highly durable films; the sap gives films oxidizable by air (oxygen). This finding corresponds to the excellent long-term durability of lacquerware and articles buried in the earth remaining in their original condition.

**Table 2. Density of Japanese sap and lacquer films at 25°C**

Film	J(S,3M)	J(S,19Y)	J(L,19Y)	J(L,1Y)
Density	1.128	1.217	1.185	1.180

S, sap; L, lacquer; M and Y are symbols of month and year

### **A way of making lacquer from sap**

Sap is stirred at room temperature for half an hour, then at 20–45°C for two to four hours in a specially designed open vessel. The conclusion of the stirring is determined by the changing color and viscosity of the sap under treatment. The lacquer film thus made usually contains 2–4% water and has an appropriate viscosity for coating.

The sap is used for the base coat on the substrate, and the lacquer for the middle and top coats. These are dried in a moist air chamber at 70–80% RH for one day.

In this process, the following developments take place: water evaporation, deposition of the polysaccharides from the water droplets in the sap, subdivision of the deposited polysaccharides into fine particles, followed by the dispersion into urushiol, grafting of urushiol onto the glycoproteins and its association with the polysaccharides (making the dispersion of the polysaccharides in urushiol easier), and urushiol polymerization. Thus, lacquer is a mixture of mono- and oligo-urushiol, fine

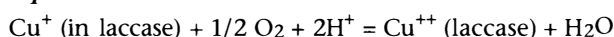
particles of the polysaccharides or their aggregates associated with the glycoproteins or urushiol-glycoproteins, laccase, stellacyanin, mono- and oligo-sugars and water.

This account is derived from the results obtained in studying (a) the laccase-catalyzed polymerization of urushiol (Oshima 1985:2613), (b) IR-spectral analysis of the glycoprotein component separated from the sap under treatment to make lacquer (Kumanotani 1981:643;1983:225), (c) SEM photographs of the dispersed polysaccharide particles in the lacquer (unpublished data), and (d) alteration of the visco-elastic properties of the sap in the lacquer-making process (Amari 1980:629).

### Drying of sap or lacquer in a humid chamber

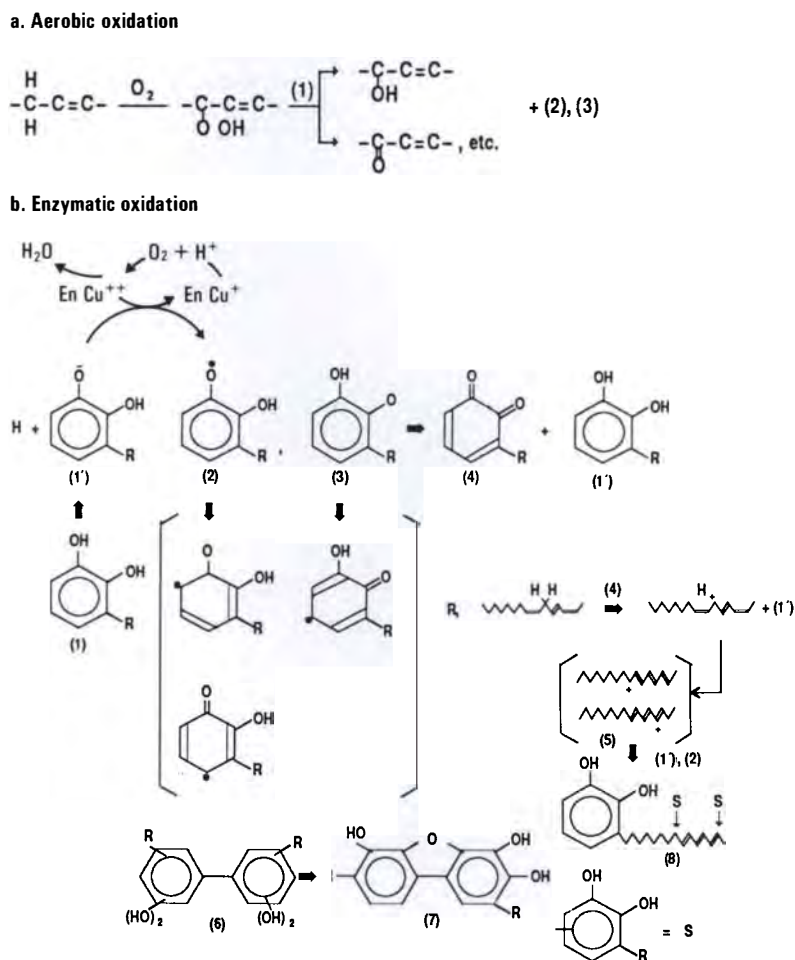
The drying of lacquer or sap in the humid chamber is initiated by the laccase-catalyzed oxidation of urushiol into a semiquinone radical (2 or 3 in Fig. 4) accompanied by the reduction of  $\text{Cu}^{++}$  into  $\text{Cu}^+$  in laccase. Subsequent or continuing oxidation of urushiol needs the oxidation of  $\text{Cu}^+$  in laccase by air (oxygen) accompanied by the formation of water:

#### Equation 1



It is easy to understand that the drying begins from the surface of the coated lacquer and is a process determined by the oxygen-diffusion rate. With the progress of drying or film formation from the upper surface to the bottom of the coated lacquer the oxygen-diffusion barrier may become larger but, when the coated lacquer layer is saturated with moisture, oxygen diffusion in the drying lacquer layer becomes easier thus supplying enough oxygen to keep the laccase copper at the active level of  $\text{Cu}^{++}$  *in situ* after its reduction to  $\text{Cu}^+$  in laccase in the drying process. This is the reason for the use of the humid chamber to complete the drying of the sap or lacquer.

Figure 4. Enzymatic and aerobic polymerization of urushiol.



In the drying process, water is produced according to Equation 1. In the initial stage of drying, polymerized urushiol (or the dried skin) formed on the surface retains the water coming up from the deeper layer in drying, with the extraction of the dispersed polysaccharides, making a higher concentration of the polysaccharides in the surface layer of the coated lacquer at the beginning of the drying. The concentration of polysaccharides in the surface layer was examined by applying the ATRIR-spectral technique (Kumanotani 1986).

Furthermore, by the same ATR technique, it is found that in the upper layer of the coated film, rigid structural units made from urushiol, biphenyl and dibenzofuran (6 and 7, Fig. 4) are more highly concentrated than in the deeper layer where the catechol nucleus-side-chain bound structure (8) is more densely packed than the others (Kumanotani 1986).

When isothermal water sorption curves were obtained for the lacquer films in certain conditions (see Fig. 5), the amount of water uptake increased and then decreased with the progress of time, indicating occurrence of the fibrous structure formation promoted by the absorbed water in the lacquer film, which may enhance the barrier to oxygen diffusion into the inside of the grains packed in the films, and contribute to the durability and the surface hardness of the lacquer films.

### Polymerization of urushiol

Two pathways are established:

#### I. Enzymatic polymerization

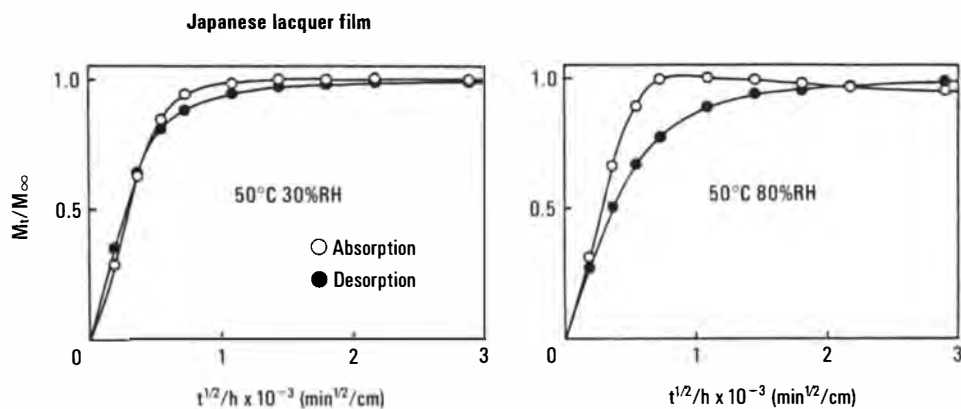
Urushiol (1) is oxidized in laccase, and the semiquinone radicals (2 or 3) formed undergo C-C coupling with each other or attack the catechol nucleus of urushiol to give diphenyl-type urushiol dimers (6), some of which may be converted to the dibenzofuran derivatives (7) through further enzymatic oxidation.

The semiquinone radicals also undergo disproportionation reactions to give urushiol (1) and urushiol-quinone (4) that may interact with the unsaturated side-chain to produce catechol-side chain-bound products (8). The catechol nucleus of these urushiol dimers can undergo further enzymatic oxidation, to give trimers, tetramers, etc., through laccase-catalyzed polymerization with urushiol or with each other.

#### II. Oxygen induced polymerization

In the lacquer-making process, the unsaturated side chain of urushiol seems to be oxidized by oxygen and the peroxides formed may undergo a reaction with the catechol nucleus or unsaturated side chain of urushiol to give semiquinone radicals (2 and 3 in Fig. 4) or cross-links between the side chains. In the former case, 2 or 3 then follows the same reaction path as when made enzymatically. Oxidative polymerization, cross-linking or degradation is significant for a lacquer or sap film kept in the air at room temperature or when drying is achieved by baking at high temperatures (110–180°C).

Figure 5. Isothermal water uptake curves.  $M_t$  and  $M$  are the amounts of water uptake in films at time  $t$  and under equilibrium conditions respectively;  $h$  is film thickness.



### **Morphological features and properties of sap and lacquer films**

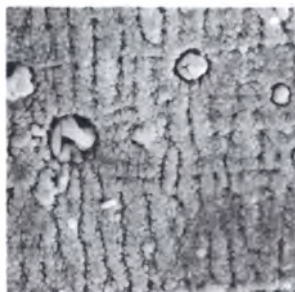
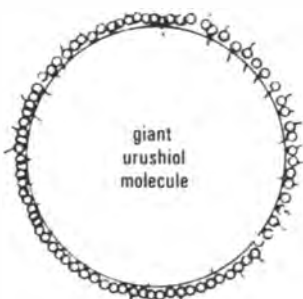


Figure 6. SEM photomicrograph of the etched lacquer film. The inside of the lacquer film is densely packed with grains 1000Å in diameter. A few larger irregular parts in the photomicrograph may come from polysaccharides that were not well pulverized in processing the sap to make lacquer.



○ polysaccharide and

⌘ polysaccharide associated with glycoprotein

Figure 7. A proposed structure for a grain in the lacquer film. Each of the grains is bound with polymerized urushiol and glycoproteins.

### **Water, sorption, and desorption**

As already mentioned, there is a heterogeneity in the surface layer: a higher concentration of the polysaccharides and the rigid urushiol dimer structure units than in the deeper layer.

It is well-known that degradation of the coated film starts from the surface by an oxygen-induced radical chain reaction, and that polyphenolic compounds are effective as chain stoppers for radical chain reactions. The dibenzofuran or biphenyl unit derived from urushiol may be one of the highly effective chain stoppers rather than the catechol nucleus in the catechol nucleus-sidechain bound structure units.

Based on the results of studying the durability of the lacquer film by dynamical property, density, etc., as a function of storage time, as well as from the SEM photographs of the etched lacquer film (Fig. 6), it is suggested that the lacquer film is packed densely with grains 1000Å in diameter, which are responsible for its excellent durability.

Each grain is composed of a wall of polysaccharides with polymerized urushiol inside, "sewn" together with the polymerized urushiol and glycoprotein moiety. The polysaccharide wall, which may absorb humidity, keeps out humidity by the effect of hydrophobic polymerized urushiol linked with the polysaccharides and glycoproteins, so resulting in the polymerized urushiol in the inside of the grain being protected from oxidative degradation (Kumanotani 1981:643, 1983:225).

On the other hand, the sap film is composed of an island (polysaccharides)-sea (polymerized urushiol) texture where the polymerized domain is without any protection from air and is easily oxidized, resulting in cross-linking, followed finally by oxidative degradation (Kumanotani 1981:643; 1983:225).

The more highly concentrated polysaccharides in the surface layer may participate in making a lacquer film with high surface hardness or with high glass transition temperature, forming a good barrier to oxygen diffusion.

When exposed to sunshine, the lacquer film may absorb sunlight and suffer from photo-oxidative degradation of the urushiol moiety binding each of the grains; the first row of the grains in the films disappears as powdery efflorescence and the second row appears as a new surface, indicating that the lacquer film is degradable out of doors but able to keep the same appearance as the original.

As may be seen from Figure 7, a phase-inversion occurs with progress of the polymerization of urushiol; the high molecular weight urushiol polymers with polar hydroxyl groups on the outside may absorb on their surface the polysaccharides or those associated with glycoproteins or urushiol grafted glycoproteins, so making a grain-structured dried film.

Indoors, it is found that light with wavelength shorter than 360 nm should be removed from the lamps used for the exhibited lacquerware in order to reduce the extent of photodegradation, which is observed as a decreasing degree of gloss of the lacquerware (Araki 1978:1). This measure is understandable, since the oligomeric urushiol isolated from a sample of lacquer showed absorption for light with wavelength shorter than 360 nm.

Lacquer contains not only a trace of water (1-4%, usually 3%) but also hydrophilic components such as polysaccharides and glycoproteins. The glass transition temperature ( $T_g$ ) of water is below  $-100^\circ\text{C}$ . Water is expected to lower the  $T_g$  of the lacquer film when it is absorbed in the lacquer, and it causes easier oxygendiffusion in films, possibly leading to promotion of oxidative degradation by air (oxygen). Furthermore, desorption of the absorbed water in equilibrium in films brings shrinkage or internal stress in the lacquerware, sometimes introducing cracks in technically reinforced lacquerware.



**Table 3. Equilibrium sorption water  $C^\infty$  (%) and diffusion constant  $D_{av}$  ( $\text{cm}^2/\text{sec}$ ) for films, *Rhus verniciflua***

Relative humidity (%)	Temperature ( $^\circ\text{C}$ )					
	30		40		50	
	$C^\infty$ (%)	$D_{av} \cdot 10^{-7}$	$C^\infty$ (%)	$D_{av} \cdot 10^{-7}$	$C^\infty$ (%)	$D_{av} \cdot 10^{-7}$
<b>Sap</b>						
30	1.5	0.78	1.2	1.55	1.3	3.13
60	2.1	0.96				
80	3.1	1.12	3.2	2.29	3.5	4.01
<b>Lacquer</b>						
30	1.3	1.16	1.0	2.52	1.1	5.26
60	1.0	1.44				
80	1.1	1.67	2.9	3.34	3.1	6.25

Based on the measured isothermal absorption and desorption curves for water under various conditions (see Fig. 5), the equilibrium water uptake and diffusion constant of water vapor in films were obtained (Table 3). It became clear that the water uptake is larger for the sap film than for the lacquer, increasing with increasing RH and measuring temperature, and it ranges between 1–4% at 30–50°C and 30–80% RH. Larger values of the diffusion constant are given for the lacquer film, indicating that this film may have favorable properties allowing it to recover an equilibrium amount of water as quickly as possible in response to alterations in temperature and humidity. This is also a very important property for the high durability of lacquer films.

From the  $T_2$  time (spin-spin relaxation time) measured by a pulse NMR for the sap and lacquer films, polysaccharides, and glycoproteins under various conditions of temperature and humidity, it was found that water is also one component of the construction of the film, and an internal stress is expected to occur on water desorption.

Consequently an equilibrium amount of water-uptake is essential in the lacquer films to keep their shape without imposition of stress, otherwise troubles can happen in lacquerware that has been kept for a long time, even though it is strengthened by application of a material reinforcing technique. Of course it should be noted that excess water over the equilibrium amount would be expected to reduce the oxygen-diffusion barrier of the polysaccharide wall of the grains in the lacquer films, promoting degradation of the films by oxygen.

## Appendix

Here is a brief description of the man-made technique established empirically on the basis of the results of studies on Japanese lacquer chemistry.

### 1. Selection of sap

Color, odor, and flow properties of sap have traditionally been an index to estimate the quality of the sap, which should be replaced by the modern analytical method already described for each constituent of the sap. Based on the film formation mechanism studied, dryability of the sap or lacquer and mechanical strength of the dried film seem to be much influenced by the content of urushiol with a triene side chain and laccase, and a balanced composition of the sap like that of the Japanese *Rhus verniciflua*.

### 2. Lacquer making process

As already mentioned, an homogeneous lacquer is made through the pulverization of the polysaccharides, followed by dispersion into urushiol; the design of the wooden vessel with stirrer for making lacquer may be important here. Heating of the sap to make lacquer, caused by friction between the stirrer and the bottom of the vessel (see Fig. 8) may diminish the activity of laccase in the sap under treatment. Too much clearance between the stirrer and the bottom of the vessel results in failure to pulverize the polysaccharides, and yields an inhomogeneous lacquer that may result

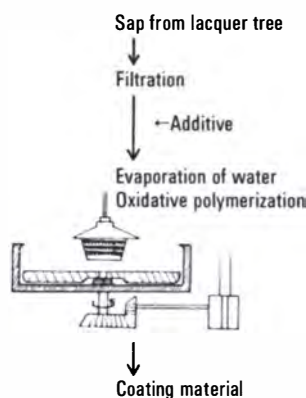


Figure 8. The process of making lacquer from sap, using a vessel equipped with a stirrer.

in defects in the dried films made by the deposited polysaccharides from water droplets in the films (Fig. 6).

### 3. Skillful coatings

The lacquer artist or craftsman should coat the lacquer thinly on the substrate, for example to a thickness of 5–10  $\mu\text{m}$ , and dry it at a temperature and humidity selected empirically. It was found in the laboratory that thickly coated lacquer needs a longer drying time than a thinly coated one, and before the complete drying of the coated lacquer the dispersing polysaccharides, particularly those with larger sizes or their aggregates, fall to the bottom layer facing the substrate, introducing a larger heterogeneity in the dried lacquer than in that made without precipitation of the polysaccharides. In addition to the surface heterogeneity already mentioned, the bottom layer of the film is rich in precipitated polysaccharides; thus the major, middle part is mainly composed of the urushiol moiety (with less of the polysaccharides), and may consequently suffer from oxidation or degradation like the oxidizable sap film with its separated polymerized urushiol and polysaccharide phases.

An example supporting this laboratory work was that of a lacquer-coated pillar of a shrine which turned white after being degraded out of doors. Moreover, even homogeneous lacquer is found to give dried films with some defects, as already mentioned. To correct these defects a second coating is required. In practice, along with the experimentally observed facts, thin-layer multicoating techniques have been established empirically by craftsmen without scientific knowledge. This is indispensable for getting durable lacquer films.

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# Glossary

**M**any of the Japanese words used in this volume appear only once and their meaning is given in parentheses in the text. This glossary contains terms which are used frequently and thus not defined on every occasion. More extensive explanations of techniques are also given.

It must be emphasized that the terminology in this field has not yet been completely standardized. The interpretations in this glossary are drawn partly from the papers themselves and partly from other sources. They should not be regarded as definitive.

The assistance of Professor Kazuo Yamasaki and Mr. Toshikatsu Nakasato is gratefully acknowledged, as well as the “List of Technical Terms” compiled during the 1985 Urushi Study Group meeting by Andreas Burmester and Toshiko Kenjo.

A glossary of specifically architectural terms appears in the article by Yoshio Hasegawa. Historical terms for stages in Chinese *kyushitsu* are given by Hirokazu Arakawa and current Japanese usage by Shogyo Ohba. The names of shells used for *raden* form an appendix to the paper by Yoshikuni Taguchi. Most of this terminology has not been repeated here.

<i>akikusa</i>	autumn plants and grasses, a typical design in Kodaiji lacquers
<i>aogai</i>	shell of abalone used in inlays ( <i>raden</i> ); literally “blue-green shell”
<i>aokin</i>	an alloy of gold and silver
<i>atsugai</i>	shells used for inlay, thicker than <i>usugai</i> ; literally “a thick shell”
<i>awabi</i>	of the genus <i>Haliotis</i> (e.g., abalone or sea-ear)
<i>bengara</i>	a red ocher pigment
<i>bon</i>	a tray
<i>bunko</i>	a document box
<i>chinkin-bori</i>	a technique in which the urushi surface is carved with a sharp instrument and the incised design is filled with gold (see also <i>qiangjin</i> )
<i>choshitsu</i>	a technique in which a thick layer of urushi is built up with many coats and a design is engraved on the surface
<i>Chusonji</i>	a temple at Hiraizumi, Iwate prefecture, noted for the richness of its lacquer decorations
<i>Coromandel lacquer</i>	lacquerware produced for the European export trade (named after the East India Company’s trading post on the Coromandel coast of southeast India); designs are cut through several layers of lacquer to the wooden base, and the spaces filled with colored lacquer and other substances
<i>danmon</i>	fine cracks on an urushi-varnished surface
<i>dei-e</i>	painting with gold or silver powder mixed with animal glue ( <i>nikawa</i> )
<i>doroji</i>	an urushi substitute made of animal glue ( <i>nikawa</i> ) mixed with powdered sea-shells ( <i>gofun</i> ) and finely ground baked clay ( <i>tonoko</i> )
<i>dozuri</i>	a technique for polishing the kind of urushi surface known as <i>roiro-urushi</i> , using a mixture of carbon powder and water, or a mixture of finely ground baked clay ( <i>tonoko</i> ) and vegetable oil
<i>dry lacquer</i>	see <i>kanshitsu</i>
<i>e-nashiji</i>	<i>nashiji</i> used to make a design rather than used as a background; literally “picture <i>nashiji</i> ”
<i>fude</i>	a brush; also a technique using a brush, as in <i>fude-sabi</i> (using a <i>makie</i> brush to apply a soft paste made from <i>sabi</i> and water)
<i>fun</i>	filings or powder, usually of metal, e.g., <i>maru-fun</i> (round powder) and <i>sai-fun</i> (fine powder)
<i>fundame</i>	a fine ground layer of gold or silver powder worked to a smooth, mat finish
<i>gai, kai</i>	a shell
<i>gami, kami</i>	paper
<i>gin</i>	silver, as in <i>gin-makie</i>
<i>gofun</i>	powdered seashells used as a white pigment or priming material
<i>gosu</i>	a round box
<i>guri</i>	a technique in which layers of different-colored urushi are applied to an object and a design is carved deeply into the surface to reveal the layered effect; the typical spiral scroll design gives the technique its name, literally “crooked ring” (see also <i>qulun</i> )
<i>hagiokoshi</i>	a technique for removing the top coating applied over shell inlay ( <i>raden</i> ) or <i>hyomon</i>
<i>hakudo</i>	white clay mixed with a thin solution of animal glue ( <i>nikawa</i> )
<i>haritsuke</i>	a simplified technique of <i>hyomon</i>
<i>heidatsu</i>	thin sheets of metal (thicker than <i>kirigane</i> ) cut into decorative shapes and applied to a lacquer base; further coats of lacquer are applied and the surface is then polished to reveal the metal
<i>hidori-urushi</i>	urushi in which the moisture is evaporated in sunlight
<i>hinoki</i>	Japanese cypress ( <i>Chamaecyparis obtusa</i> )

<i>hiramakie</i>	<i>makie</i> decoration in very low relief, i.e., only the thickness of the final urushi coating raises it above the surface; literally “flat sprinkled picture”
<i>hirame-fun</i>	flat flakes of metal used for <i>makie</i> ; literally “flat-eye dust”
<i>homen</i>	a surface prepared by laminating cloth using urushi as the binder
<i>hyomon</i>	thin metal plates (thicker than <i>kirigane</i> ) are cut into a pattern or design, laid on the urushi, and the surface varnished again with urushi; then the top coating of urushi is polished, revealing the metal design, set flush into the urushi (see also <i>heidatsu</i> )
<i>ikakeji</i>	lacquerwork coated with a densely applied fine gold power
<i>inro</i>	a small, compartmentalized container, originally for seals, but also used for medicines and other small objects; the boxes are held together by a cord and closed by a bead ( <i>ojime</i> ); the top of the cord runs through a toggle ( <i>netsuke</i> ) by which the <i>inro</i> is hung from the sash ( <i>obi</i> )
<i>iro</i>	literally “color”; thus <i>iro-urushi</i> is colored urushi
<i>japanning</i>	a varnish coating used to imitate Oriental lacquerwork; the term was first published in <i>A Treatise on Japaning and Varnishing</i> by John Stalker and George Parker, London (1688)
<i>jigatame</i>	ground coating of <i>jinoko</i> and urushi
<i>jikiro</i>	a food container
<i>jinoko</i>	clay that is baked, ground, and screened; coarser than <i>tonoko</i> (see also <i>Wajima</i> )
<i>jitsuke,</i> <i>jizuke</i>	a process in which <i>jinoko</i> is applied with a spatula
<i>jubako</i>	a nest of boxes, or stacking boxes
<i>kaizuka</i>	a shell mound
<i>kamakura-</i> <i>bori</i>	wood carved and then thinly coated with urushi (as opposed to true carved urushi, e.g., <i>guri</i> )
<i>kanagai</i>	lacquerware inlaid with gold or silver leaf
<i>kanshitsu</i>	a technique for coating an object using layers of cloth soaked with urushi and pressed over a clay and wooden form that is later removed ; also known as dry lacquer
<i>karamushi</i>	ramie; an Asian perennial plant ( <i>Boehmeria rivea</i> ) of the nettle family
<i>katakata-</i> <i>haku,</i> <i>katakata-nui</i>	fabric decoration in which one surface is decorated with gold foil ( <i>haku</i> ) and the other with gold embroidery ( <i>nui</i> ); the effect is similar to that of <i>katami-gawari</i>
<i>katami-</i> <i>gawari</i>	the design or pattern on one half of an object is different from that on the other half—a deliberate contrast
<i>katawagu-</i> <i>ruma</i>	a traditional design showing a wheel half-immersed in water
<i>kawari-nuri</i>	a decorative technique in which cracks are made deliberately in the surface of colored urushi
<i>kebori</i>	hairline engraving
<i>kiji</i>	a wooden substrate
<i>kijigatame</i>	the consolidation of the wooden substrate
<i>kijiro-urushi</i>	transparent urushi without the addition of a drying oil
<i>kin</i>	gold
<i>kingin-e</i>	decoration using gold and silver powder; literally “gold-silver picture”
<i>kinma,</i> <i>kimma</i>	a technique in which lines are engraved on the urushi surface and colored urushi is embedded in the incisions and burnished
<i>kinmakie</i>	a type of gold and urushi surface achieved with fine gold powder applied in the <i>makie</i> technique, remarkable for its luster
<i>kintai</i>	urushi applied to a metal substrate

<i>kirigane, kirikane</i>	<i>makie</i> design made from tiny pieces of sheet-gold, gold foil, or gold wire (in contrast to gold powder) applied with urushi ; literally “cut gold”
<i>kiriko</i>	a paste made of <i>jinoko</i> and/or <i>tonoko</i> , water, and raw urushi
<i>kiri-mon</i>	a decorative motif depicting the leaves and flowers of the paulownia tree
<i>ki-urushi</i>	raw urushi
<i>Kodaiji-makie</i>	a style of lacquer decoration associated with the Kodaiji temple, Kyoto, fashionable in the Momoyama and early Edo periods
<i>kokuso</i>	a thick paste of kneaded urushi with various admixtures, typically clay powder and sawdust, sometimes hemp fiber and incense powder, used to cover the wooden foundation before the lacquering process
<i>koshoku</i>	antiquing; literally “old color”
<i>koto</i>	a stringed musical instrument, the Japanese harp or zither
<i>kura</i>	a saddle
<i>kuro</i>	black; <i>kuro-urushi</i> is made by mixing transparent urushi with an iron compound
<i>kurome</i>	the process of making transparent urushi from raw urushi, in which the water contained in raw urushi is evaporated with gentle heating
<i>kuro-nuri</i>	to coat with black ( <i>kuro</i> ) urushi
<i>kyushitsu</i>	the sequential application of urushi, from the ground coating to the surface coating
<i>magemono</i>	bent work
<i>magewa</i>	thin strip of wood used in making <i>magemono</i>
<i>makie</i>	metallic powder, usually gold, is sprinkled on a wet lacquer surface to form a picture or design; literally “sprinkled picture”
<i>makie-fude</i>	a brush used for <i>makie</i>
<i>makie-fun</i>	filings or powder, usually of metal, used for <i>makie</i>
<i>makie-hanashi</i>	<i>makie</i> that is not polished—the gold powder is simply sprinkled on without subsequent treatment; <i>hanashi</i> means “to leave alone”
<i>mitsuda-e</i>	oil painting with pigments bound with oil alone or a mixture of oil and lacquer, with a drying agent
<i>mugi-urushi</i>	urushi with adhesive properties made of raw urushi, water, and wheat or rice paste, sometimes with other admixtures
<i>murasaki</i>	purple; <i>murasaki-urushi</i> is a method of making purple-colored urushi
<i>nakanuri</i>	the intermediate coating(s)
<i>nashiji</i>	flakes of gold of irregular size and shape are set at differing angles in a bed of wet urushi and a further coating of urushi is applied; literally “pear skin”
<i>natsume</i>	a tea-powder container, named for the <i>natsume</i> fruit, which it resembles in shape
<i>Negoro-nuri</i>	the lacquerware at the Negoro temple was originally red but the surfaces became worn in use and the underlying black showed through in places; this effect was later deliberately imitated
<i>nerigaki</i>	a mixture of urushi and gold filings
<i>nerimono</i>	a paste, typically used for molding shapes
<i>nikawa</i>	animal glue; <i>sanzenbon nikawa</i> is a kind of animal glue in stick form
<i>nori</i>	rice glue; <i>nori-urushi</i> is raw urushi admixed with rice paste
<i>nunokise</i>	a technique in which cloth is applied to a substrate with <i>nori-urushi</i>
<i>nuri</i>	literally “coating,” especially with urushi; also used to refer to lacquerware, e.g., <i>Wajima-nuri</i>
<i>nuritate-shiage</i>	a final coating; literally “top coating with oil luster”
<i>ohaguru</i>	ferric tannate



<i>okigai</i>	small pieces of shell used like mosaic
<i>qiangjin</i>	Chinese term for incised decoration filled with gold (see also <i>chinkin-bori</i> )
<i>qiangyin</i>	Chinese term for incised decoration filled with silver
<i>qulun</i>	Chinese name for <i>guri</i> ; <i>xipi</i> , <i>tixi</i> also used
<i>raden</i>	shell inlay, especially with mother-of-pearl
<i>rankaku-nuri</i>	finely broken eggshells applied to a wet urushi surface to form a design; literally “egg coating”
<i>rantai</i>	bamboo woven to form a substrate for urushi; <i>rantai-shikki</i> are vessels with a bamboo base
<i>roiro-nuri</i>	a mirrorlike, deep black lacquer finish achieved by the multiple application of thin layers of <i>roiro-urushi</i> , each polished to a high finish
<i>roiro-urushi</i>	a form of urushi achieved by adding an iron-based pigment to high-quality raw urushi to give a black color
<i>rokuro</i>	a lathe or a potter’s wheel
<i>sabi</i>	raw urushi mixed with finely ground baked clay ( <i>tonoko</i> ), used for the ground layer; other substances may be added
<i>saku</i>	“made by” (as in <i>fecit</i> )
<i>sakura</i>	the cherry tree or its blossom
<i>se</i>	a Chinese zither
<i>shikki</i>	lacquerware
<i>shippi-bako</i>	a leather box
<i>shitaji</i>	foundation layer; literally “underneath ground”
<i>shitajigatame</i>	ground consolidation ( <i>numokise</i> + <i>jigatame</i> )
<i>shitanuri</i>	the base coating(s)
<i>Shosoin</i>	the eighth century Imperial Treasure House at Nara
<i>shu</i>	cinnabar
<i>shumidan</i>	a dais for a Buddhist image; an altar
<i>shunkei-nuri</i>	a technique of applying transparent urushi over wood grain so that the beauty of the natural wood pattern shows through; there are several regional variants
<i>soku</i>	an older term for dry lacquer (see <i>kanshitsu</i> )
<i>sozo</i>	clay sculpture technique
<i>suki-urushi</i>	a general term for all types of transparent urushi
<i>sumi-e togidashi</i>	a style of <i>togidashi</i> imitating an ink-painting
<i>suri-urushi</i>	raw urushi thinned with a diluent or solvent such as camphor
<i>suzuribako</i>	a writing box
<i>takamakie</i>	high-relief <i>makie</i> ; a technique in which the design is built up and modeled in a mixture of lacquer and charcoal or clay dust
<i>tebako</i>	a small ornamental box for toiletries; cosmetic box
<i>togidashi</i>	<i>makie</i> technique in which the completed low relief ( <i>hiramakie</i> ) design and its ground are covered in further layers of lacquer, which are then polished down until the design reappears flush with the new ground
<i>tonoko</i>	a finer version of <i>jinoko</i> ; literally “grinding powder”
<i>torii</i>	a Shinto shrine archway
<i>tsubuoki</i>	placing pieces of gold or silver on an urushi surface to obtain a particular decorative effect
<i>tsuikoku, tsuishu</i>	techniques similar to <i>guri</i> , in which layers of lacquer—black in the case of <i>tsuikoku</i> , red for <i>tsuishu</i> —are carved in elaborate designs
<i>tsunoko</i>	calcined deer-horn used in polishing

<i>urauchi</i>	Japanese paper applied to the back of cloth for reinforcement
<i>urumi</i>	black urushi admixed with iron oxide red or vermilion; alternatively, urushi colored with vermilion is further admixed with lamp black
<i>urushi</i>	the sap of <i>Rhus verniciflua</i> and other trees of the Anacardiaceae family; also used as a general term for the processed sap
<i>urushiburo</i>	a wooden box kept permanently moist by sprinkling with water, in which lacquered objects are placed to harden; also called <i>shimeshiburo</i>
<i>urushi-e</i>	a technique of true lacquer painting, used especially during the Edo period, in which colored pigments are dissolved in urushi
<i>urushikaki</i>	sap collectors
<i>urushiol</i>	a mixture of phenol derivatives, the main component of urushi
<i>usugai</i>	shells for inlay thinned by grinding; literally “thin shell”; their thickness is 8.25 mm per 100 sheets
<i>uwanuri</i>	the final coating(s)
<i>vernis Martin</i>	a varnish finish used by Guillaume Martin and his brother in their Paris workshop to imitate urushi, c. 1730
<i>Wajima</i>	a town in Toyama prefecture noted for its production of ground baked clay ( <i>jinoko</i> ); the clay is formed into bricks about 4 cm in diameter and 1.5 cm high, dried, and baked; the baked clay is ground and classified in order of decreasing particle size: <i>ichi-henji</i> , <i>ni-henji</i> , <i>san-henji</i> , etc.
<i>Wajima-nuri</i>	lacquerware using a technique similar to <i>chinkin-bori</i> ; clay from Wajima is mixed with urushi, giving a smooth strong surface for carving
<i>wan</i>	a bowl
<i>warigai</i>	a technique for breaking shells that are first stuck to a paper backing
<i>washi</i>	Japanese paper
<i>zonsei</i>	a technique in which the outline of the design drawn in colored urushi is line-engraved and the incisions are filled with colored urushi or gold dust



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