

Studies in Conservation



ISSN: 0039-3630 (Print) 2047-0584 (Online) Journal homepage: http://www.tandfonline.com/loi/ysic20

The reproduction of realistic samples of Chinese export lacquer for research

Marianne Webb, Michael R. Schilling & Julie Chang (張倚竹)

To cite this article: Marianne Webb, Michael R. Schilling & Julie Chang (張倚竹) (2016) The reproduction of realistic samples of Chinese export lacquer for research, Studies in Conservation, 61:sup3, 155-165, DOI: <u>10.1080/00393630.2016.1227116</u>

To link to this article: https://doi.org/10.1080/00393630.2016.1227116

_	
\mathbf{n}	
U	

© 2016 The J. Paul Getty Trust.



Published online: 15 Dec 2016.

Submit your article to this journal \square

Article views: 533



View Crossmark data 🗹

Supplementary issue paper The reproduction of realistic samples of Chinese export lacquer for research

Marianne Webb¹, Michael R. Schilling², Julie Chang (張倚竹)²

¹Webb Conservation, Ottawa, Canada, ²Getty Conservation Institute, Los Angeles, CA, USA

Three late-eighteenth-century to early-nineteenth-century objects made from Asian lacquer were analyzed using histochemical staining of cross-sections and pyrolysis-gas chromatography-mass spectrometry, and found to include laccol, and perilla oil and cedar oil, in contrast to urushiol alone, commonly used as an analytical marker for Asian lacquer. Sample set based on urushi made from laccol, and varied amounts of perilla oil and cedar oil were created and light aged in a xenon arc weatherometer, further aged in different levels of relative humidity, while physical changes were monitored by means of pH, gloss measurements, and autofluorescence during aging. The pH was dependent on initial composition. The study gave new understanding of autofluorescence in lacquers, and made clear that samples for experiments must include urushi, laccol, and thitsi, which have physical and chemical differences. The hypothesis that urushi has superior aging characteristics to laccol is not consistent with the results. The experiments also demonstrated that other ingredients constituting major additives are equally important to the behavior of lacquer as it ages.

Keywords: Laccol, THM-Py-GC-MS, Chinese export lacquer, Urushi, pH, Autofluorescence

Introduction

The process of object examination, analytical research to identify materials, and reproduction of accurate replicas has been used successfully to study paintings and coatings applied to western works of art. However, this process has not been fully applied to Asian lacquer. For the most part, studies of the aging and behavior of Asian lacquer objects have focused on identifying urushiol (from Toxicodendron vernicifluum). Research on Asian lacquers at the Getty Conservation Institute (GCI) has revealed a naïveté in this approach. Numerous additives and lacquer mixtures may be identified using pyrolysis-gas chromatography-mass spectrometry with derivation by tetramethylammonium hydroxide (THM-Py-GC-MS) (Heginbotham et al., 2008). Moreover, peak areas reported for the various marker compounds detected provide a rough estimate of the relative proportions of the lacquer raw materials identified in the samples, but not actual weight percentages (Heginbotham et al., 2016). Ultimately, the research has demonstrated that Asian lacquer is far more complex than was previously believed.

Correspondence to: Marianne Webb, Webb Conservation, Ottawa, Canada, Email: mw@mariannewebb.com

Analysis

In the present study, three Chinese export lacquer objects were analyzed: an eighteenth-century tea caddy, a screen dated to ca.1820, and an earlynineteenth-century sewing box. These three objects are presumed to be typical of the Chinese export pieces found in numerous private and public collections. Immensely popular in the eighteenth and nineteenth century, these factory-produced Asian lacquer objects were widely distributed throughout Europe and the Americas. Analysis was carried out using histochemical staining of cross-sections and THM-Py-GC/MS analysis of the lacquer layers. Due to difficulties in removing microsamples, it was not always possible to isolate each individual layer, so some samples consisted of several adjacent layers.

Cross-sectional samples revealed that the layering structure was quite similar in all three objects (see Figs. 1 and 2 and Table 1). The wooden substrate was covered with a ground layer, followed by a layer of fibers and another layer of ground. Analysis of the ground layers of the screen indicated that the two primary binders were blood and perilla oil with a small amount of starch.

In each of the three Chinese export objects, only two or three lacquer layers were visible. Nevertheless, the

© 2016 The I. Paul Getty Trust.

This is an Open Access article distributed under the terms of the Creative Commons Attribution-NonCommercial License (http://creativecommons.org/licenses/ by-nc/4.o/), which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited. ceived July 2015; revised paper accepted August 2016 VOL. 61 Studies in Conservation 2016 DOI 10.1080/00393630.2016.1227116

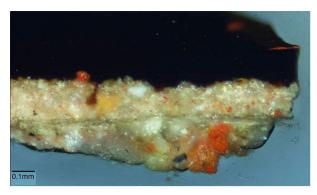


Figure 1 Cross-section of the tea caddy viewed under visible illumination.



Figure 2 Cross-section of the tea caddy viewed under UV illumination.

Table 1	Description of the layers observed in the cross-
section	from the Chinese tea caddy

Layer	Name	Description						
I	Surface coating	A very thin layer of surface coating that fluoresced differently from the black upper lacquer layer (this layer may be the result of light damage)						
Н	Gold	Located on top of every surface						
G	Black upper lacquer	Dark, small particles that may be pigment						
F	Black lower lacquer	Dark, small particles that may be pigment						
E	Coating (lacquer?)	A thin layer of coating applied onto the second ground layer that can only be seen under UV light						
D	Second ground	Less coarse than ground layer B, but in common with that layer also contains a mixture of different materials						
С	Fiber layer	A layer of fibrous material located between the two ground layers. It has a uniform thickness						
В	Ground	Coarse textured layers containing a mixture that includes a finely divided orange material, blue crystals and colorless crystals. These can be differentiated easily under UV illumination and may be vermilion, ash and an earth pigment						
А	Wood?	Not visible in photomicrograph						

lacquer layers on all three objects were found to contain laccol from *Toxicodendron succedaneum* and not urushiol, although urushiol was identified in the top lacquer layer of the screen. Recent studies have shown that laccol use in Chinese export lacquer was quite common (Heginbotham *et al.*, 2016). It is difficult to differentiate laccol from urushiol in Chinese historical records, because the Chinese identify them using the same character. Fortunately, the Ming government's tributary list indicates lacquer as one of the tributes from Jiaozhi, the historical name for Vietnam during the Fourth Chinese domination (Institute of History and Philology, 1962). Based on the above information, it is reasonable to say China had access to laccol lacquer in the fifteenth century.

Drying oils also formed a major ingredient in the lacquer layers of the three objects. Perilla oil was identified in the upper lacquer layers of the tea caddy and sewing box, but in the screen the ratio of palmitic acid to stearic acid was 4.5, which fell slightly above the range for typical drying oils used in China. Perilla oil is one of the most common types of drying oil found in historical documentation. It has been associated with lacquer manufacturing in many historical texts, such as the Ben cao shi yi (A Supplement to Materia Medica) written in the Tang Dynasty (618–907 CE), so its presence is not unusual (Chen & Shang, 2002). The other important component in all three objects was cedar oil, which is consistent with earlier studies (Heginbotham et al., 2008,2016).

Preparation of samples

The second part of this study was an assessment of the role that the type of Asian lacquer (mixed with additional constituents) plays in determining the physical characteristics and aging behavior of objects.

In order to compare the behavior of the laccolbased and *urushi*-based lacquers, six sets of samples based on *urushi* and five sets based on laccol were made. All 11 sample sets followed the same simplified traditional lacquer process. One goal was to compare the surface characteristics, so it was essential to reduce the differences in the substrate and preparatory layers. It was also important to eliminate other factors in aging such as dimensional changes in the substrate. For this reason, the substrate chosen was a 3 mm thick, six-layer birch plywood from Finland.

Raw *urushi* was used in each step of the preparation of the *urushi* samples and raw laccol, both low and better quality mixed, was used for the samples of Chinese export type lacquer. The boards were cut and then sealed with raw Asian lacquer and dried using a wood *furo* (brazier or hearth) at a relative humidity (RH) around 80%. The ground layer was made by mixing the appropriate raw

lacquer with *tonoko* (coarse, unbaked clay) from Tokyo and applying this to the surface using a spatula. A single ground layer was applied to both sides and, after drying, the surface was polished to a smooth finish using a sequence of 600, 1000, and 1500 grade artificial stones. Once smooth the boards were again sealed with another thin layer of raw lacquer. After sealing, three layers of the appropriate Asian lacquer test coating were applied to one side of the board. The first two layers were abraded using the finest grade of artificial stone or sandpaper. The top layer was a brush coat that was not given a final polish.

The analytical results from the export objects were simply a starting point for formulating the process to make Chinese export lacquer replicas. The working properties of the laccol-based lacquer, purchased in Taiwan, proved to be quite different from urushiol. The raw lacquer used to seal the ground layers seemed to start drying soon after application, became quite viscous within a few minutes and left prominent brush stokes after drying. The unadulterated, processed black lacquer behaved as a diluant fluid making its application with a brush difficult, but once in place it leveled satisfactorily.

The addition of oils considerably improved the working characteristics. Although the analytical results showed peak areas of greater than 50% oil, other studies in Japan (Kenjo, 1977) demonstrated that if the oil content exceeded 40% the urushi would separate. Accordingly, a conservative addition of oil was chosen for the sample boards. Two formulations were tested; in the first, black laccol lacquer processed in Taiwan was mixed with 15% perilla oil and 5% cedar oil by weight (sample CEL#1). This formulation lowered the viscosity and allowed the lacquer to be spread with no resistance. The second formulation used a black laccol lacquer with oil already incorporated during processing. Cedar oil (10% by weight) was added, which again lowered the viscosity and improved the working characteristics (sample CEL#2).

Although the addition of the oils increased the gloss on drying, the unadulterated laccol lacquer still possessed a higher gloss than unadulterated black *urushi* (Fig. 3). The high gloss finish of the laccol lacquer greatly reduced that production time as it reduced the need to spend time polishing. It seems likely that the use of laccol lacquer diluted with oil made the final product less expensive in terms of both material and production costs. These differences in the chemical and physical makeup of Chinese export lacquers will no doubt be reflected in their aging characteristics.

A second phase of analytical work set out to determine if the analytical results from the laccol sample boards mirrored those from objects. Table 2 lists the

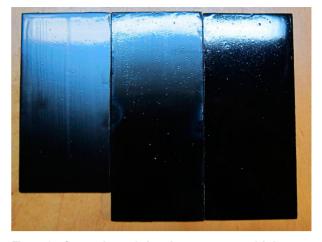


Figure 3 Comparison of gloss between types of Asian lacquer: (left) *urushi*; (center) unadulterated laccol lacquer; and (right) laccol lacquer with cedar and perilla oil. Visible bubbles are a result of brush quality and appear in all samples.

objects that were studied and the peak areas for the various marker compounds that were detected in these and the 11 sample boards. A comparison of the major ingredients gives an idea of how successfully the analytical results had been translated into the recipes used for the experimental samples (Fig. 4).

In the two layers of the Chinese export lacquer tea caddy that were analyzed, relatively low amount of anacards was detected (13.4 and 16.8%) with oils contributing 36–37%. The sample of laccol lacquer from the screen contained around 62% oil and approximately 11% resin and carbohydrate. The analytical results for these experimental samples and results from other published work show that there is a range in the amount of materials found. Although the sample boards also contain the same classes of material as the objects, none exactly matched the composition of the two objects studied. All the boards contained lower levels of carbohydrates and resins than were found in the objects, which may be a result of comparing the lacquer in aged objects to that in new sample boards.

The *urushi* sample boards, labeled U1– U6, represent six commercially available products covering a range of formulae from different sources and made for a variety of purposes. No proteins were detected in the *urushi*-based lacquers and the levels of carbohydrates were lower than in the laccol-based lacquers. Samples U1 and U2 are both black lacquers colored by the addition of iron particles, which were then filtered out after reacting with the *urushi*. The *urushi* used in U1 originated in China but was processed in Japan while U2 was harvested and processed in Japan. Both contain urushiol along with native fatty acids and neither have any added oils. They differ in the ratio of anacard to oil, with the lacquer of Chinese origin having a higher anacard content.

Object or sample	Description of lacquer	Laccol	Urushi	Oils	Oil type detected	Protein	Carbohydrates	Resins	Other	pH @ four weeks	Change in gloss at 60°
Chinese 1820 screen: upper layers	Black lacquer		5.8	84	Tallow tree oil	0.1	2.4	4.5	3.3		
Chinese 1820 screen: lower layer	Black lacquer	10.7		62.3	Perilla	0.1	11.5	11.1	4.2		
Chinese tea caddy: lower layer F	Black lacquer	13.4		35.9	Perilla	0.3	18.4	27.4	4.8		
Chinese tea caddy: upper and lower layers F & G	Black lacquer	16.8		36.7	Perilla	0.4	8.1	33.7	4.3		
L1 CEL #1	Black laccol + 15% perilla + 5% cedar oil	16.3		79.5	Linseed or perilla	0	3.2	1	0	4	44
L2 CEL #2	Black with oil + 10% cedar oil	25.9		68.5	Tung or linseed	0.2	0.7	4.1	0.7	4.66	39
L3	Black laccol lacquer	40		36.7	Tung or linseed	0	4.1	16.8	2.3	4.31	40
L4	Transparent laccol lacquer	59.9		28.1	Linseed or perilla	0.3	5.7	1	5	3.6	33
L5 CEL#1	CEL#1 on Chinese ground- tung oil, protein glue, starch and <i>tonoko</i>	14.9		78.3	Perilla or linseed	0	2.6	2.2	2	4.7	47
U1	Chinese black lacquer processed in Japan		80.2	17.1	Native fatty acids	0	0.2	0	2.5	4.13	42
U2	Japanese black lacquer		64.7	34.4	Native fatty acids	0	0.5	0.1	0.3	4.27	39
U3	Japanese kijiro transparent lacquer		70.9	26.4	Native fatty acids	0	0.1	0	2.6	3.6	31
U4	Japanese black lacquer with oil: from Chinese <i>urushi</i>		24.4	67.3	Perilla or linseed	0	0.1	5.7	2.6	3.58	65
U5	Chinese red lacquer: iron oxide pigment		36.1	61.8	Linseed or perilla	0	0.4	1.2	0.5	4.28	79
U6	Chinese red lacquer: organic pigment + barium sulfate		50.5	46.2	Linseed or perilla	0	0.1	0	3.3	3.6	52

Table 2 Details of the four samples from lacquer objects and 11 sample boards with the major ingredients identified by THM-Py-GC-MS



Figure 4 Labeled sets of completed sample boards: from left to right L1 to L4 and U1 to U6.

Sample U3 is a transparent Japanese lacquer known as *kijiro* with 70% Anacard to 26% native fatty acid. All of the other *urushi*-based coatings had varying amounts of linseed or perilla oil added. The peak areas of the oil marker compounds ranged from 46 to 67%, with the native fatty acid content likely representing 20– 35%, or roughly half of the total amount of oil indicated. Sample U3 was a black lacquer originating in China but processed in Japan while the two red lacquers U5 and U6 were prepared in China for sale in Japan.

Artificial aging

Artificial aging of the samples was carried out to determine whether the formula made a difference to behavior. It has been stated that pure *urushi*, without any addition of oil, is most resistant to light and the other affects of aging (Yamashita & Rivers, 2011).

The choice of methods for artificial aging relied heavily on past research, particularly that conducted by Brenda Keneghan, Carolyn McSharry, and Judith Thei as part of the Mazarin Chest project, Victoria and Albert Museum, London, which was key in determining the protocols for aging. Several different lamps have been studied for the artificial aging of Asian lacquer (McSharry, 2009; Keneghan, 2011) and for the experiments described here an Atlas weatherometer with a water-cooled xenon arc lamp was chosen for its ability to control the temperature and RH during exposure.

The microcracking seen on the surface of naturally aged lacquer is a result of changes in RH after light damage has occurred. The light-degraded layer swells and shrinks at a different rate to the undamaged surface beneath, and the differential tension that is created as result is relieved by the formation of cracks (Thei, 2011; Keneghan, 2011). The first approach was to combine the light and moisture aging, but after trial runs it was found that the best approach was to separate the two processes.

The light source in the Atlas weatherometer at the GCI used in the artificial aging of the samples boards was filtered using a sodium borosilicate inner filter and a soda lime glass with a CIRA (IR-reflecting) coating as the outer filter. This combination aims to replicate the spectra of natural light through window glass (Feller, 1994). The lamp was run at 0.5 W m^{-2} , with the black panel temperature set at 50 °C, the chamber temperature at 50 °C and the RH at 50%. The temperature was maintained at this relatively low level, since Takahashi's research (Takahashi, 2013) into the thermal degradation of Japanese lacquer found that the first small changes to the molecular structure occur at 65 °C (although major deterioration does not begin until 250 °C).

Unfortunately, running the experiments at these settings necessitated the addition of water to achieve the desired RH. The Atlas weatherometer uses an ultrasonic nebulizer to produce humidity and a mist of fairly large water droplets is produced beneath the bottom of the chamber and distributed by air flow. When Asian lacquer is degraded by light, the surface is very water sensitive and in the initial experiments the mist caused 'pock marks' on the lacquer surfaces. The solution was to fit the sample holders with soda lime glass to prevent water from touching the lacquer surface. Because the four initial sets of sample boards were compromised, a fifth set was used for the aging tests.

The samples received 259 kJ over 144 hours during each week; for convenience, this is referred to as a oneweek exposure. The samples were covered with aluminum foil and a section of foil was removed after each week of light exposure for a total of four weeks. This allowed for a comparison of the changing physical characteristics over the four-week period.

After light aging, the samples were exposed in a Thermotron climatic chamber to four cycles of 24 hours at 20% RH followed by 24 hours at 95% RH. At a later stage in the experiment, one set of sample boards that had been exposed to light for six weeks at 0.5 W m⁻² in the presence of water droplets was exposed to four cycles of one week at 22% RH followed by one week at 80% RH. This slower, less extreme process produced more natural patterns of microcracking, which confirms the work by Keneghan (2011) (Fig. 5).

Results and discussion

рΗ

The pH measured in this study reflects the acidity of the water-soluble degradation products from the deteriorated lacquer rather than the lacquer itself. Previous studies that measured pH focused either on a few objects or on urushi samples (Schellmann & Rivers, 2005; Thei, 2011), and no study to date has examined the change in pH with increased exposure. As a result, the hypothesis that acidity increases with exposure to light has remained unchallenged. In this study, the pH of the degradation products was measured over time from a one-week exposure to 0.5 W m^{-2} (259 kJ) to a four-week exposure (1032 kJ). The pH after four weeks was also measured in two different sets of samples, the first set exposed to water in the Atlas weatherometer, while the second set was protected from water droplets during exposure.

The pH was measured by applying chromatography paper wetted with deionized water (pH 6.5). The

paper samples were all cut to the same size and excess water was removed by blotting before it was applied to the lacquer surface for one minute. The pH was measured using a Horiba hand-held pH meter. Because the pH measurement of surfaces can be inaccurate, the measurements were taken four times using different meters. Despite a two-point calibration prior to measurement, each meter gave a different reading and the pH varied by as much as pH 2 between the highest and lowest meter readings. However, it still proved possible to discern a consistent pattern in the change in pH readings across all the meters.

Other studies have indicated that the pH of new lacquer is around pH 5 (Schellmann & Rivers, 2005). In the study reported here, however, the readings from the new lacquer samples were identical to those for paper and water alone. In theory, any water-soluble materials in newly cured Asian lacquer are bound tightly into the polymerized matrix and will not contribute to a change in the surface pH. However, a measurable change in pH could be seen in readings taken from a sample that had been exposed to 0.33 W m^{-2} for 12 hours.

Plots of pH versus exposure time for the 11 different *urushi* and laccol sample boards clearly show that after the initial week of exposure the pH does not drop greatly with increased light exposure (Fig. 6). Measurements of each sample over the succeeding three weeks varied little and were well within the margin of error. One unexplained phenomenon occurred in the case of five samples sets, where the pH first decreased then increased during the final week of exposure. The relative stability of the pH over time is not surprising since the production of acidic compounds is not auto-oxidative but purely

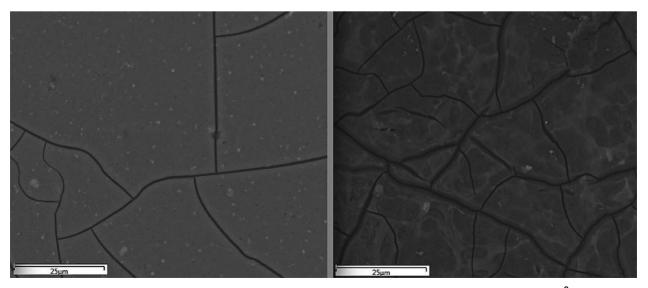
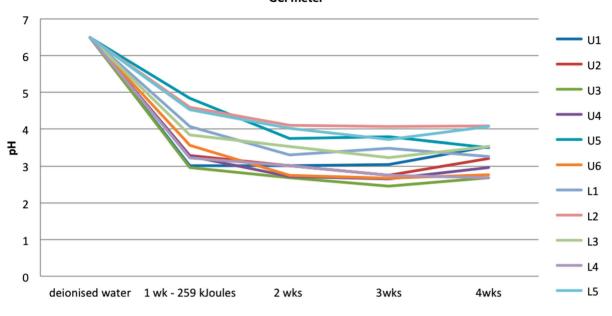


Figure 5 A comparison of cracking patterns: (left) Chinese export lacquer formula L2 after exposure to 0.5 W m⁻² for four weeks and eight days of RH cycling of 24 hours at 20% RH followed by 24 hours of 95% RH; and (right) sample L2 after exposure to two months of RH cycling at RH of 85% for a week followed by a week at 22% RH.



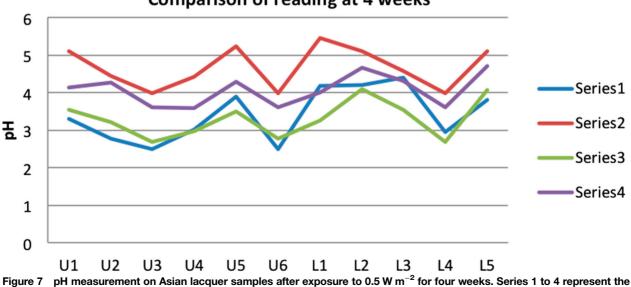
Asian lacquer 'dry' set -pH / light exposure GCI meter

Figure 6 pH measurements over time for Asian lacquer samples that were exposed to light at 0.5 W m⁻².

related to light exposure, so that the lower layers, which are not exposed to light, do not degrade (Ogawa *et al.*, 1998).

Plots of pH versus sample type show some interesting patterns (Fig. 7). The transparent *urushi* and transparent laccol without oil had the lowest pH, followed by the sample colored red with an organic pigment. These low pH readings may have their origin in the transparency of the samples, which allows light to penetrate further into the lacquer, causing greater degradation and releasing materials that increase the acidity. For the red samples, it may be that the organic pigment provides very poor protection of the lacquer. The four highest pH measurements were recorded for Chinese *urushi* processed in Japan (U1), red *urushi* pigmented with iron oxide (U5), black laccol with oil plus cedar oil (L2), and Chinese black laccol lacquer with 15% perilla and 5% cedar oil on a Chinese type ground (L5). The element common to all these lacquer was that they were colored by the addition of iron or with an iron-containing pigment.

These figures correspond to the pattern of the pH measurements made on the Chinese screen where a pH of 3.9 was recorded in the areas that utilized a transparent lacquer on the rocks and 4.7 in the plain black background.



Comparison of reading at 4 weeks

Figure 7 pH measurement on Asian lacquer samples after exposure to 0.5 W m^{-2} for four weeks. Series 1 to 4 represent the measurements taken on four different calibrated pH meters.

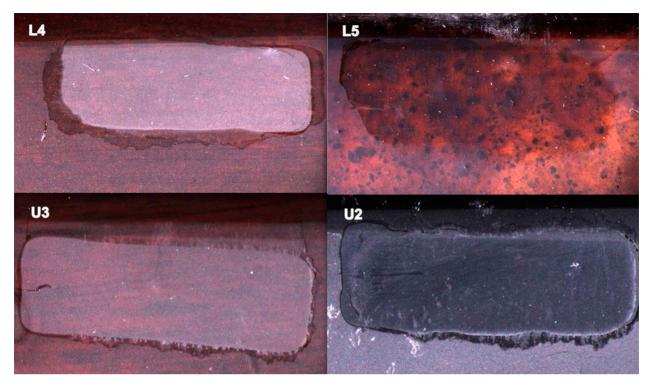


Figure 8 Marks remaining on surface after pH measurement on lacquer samples L4, L5, U3, and U2. The two transparent lacquers are on the left and the two initially black lacquers are on the right.

This study showed that the pH is clearly related to the initial formula; the transparent lacquer without added oil has the lowest pH, which would indicate that more acidic compounds have formed. It should be noted that the measurement of pH on Asian lacquer is destructive, as in every case a mark remained on the lacquer surface where the extraction of material left voids (Fig. 8). In some cases, the damage is not visible to the naked eye but is readily observed under magnification.

Gloss

The measurement of gloss has been used to gauge the extent of light exposure in a few studies (Schellmann & Rivers, 2005; McSharry, 2009). The gloss of the sample boards in the current study was measured using a Rhopoint IQ gloss meter at 20°, 60°, and 85°. Two readings were made on every sample before aging and four readings were made after exposure to light and the short period of RH cycling. The readings before and after ageing were averaged and used to calculate the change in gloss by subtraction; the results for measurement at 60° are presented in Table 2.

The gloss clearly decreases with exposure to light. A comparison of the initial gloss with the gloss measured after four weeks of light exposure reveals that the change in gloss is related to the lacquer formula. The transparent *urushi* and laccol samples had the lowest changes in gloss after exposure. The addition of oil seems to result in a slight increase in the loss of gloss, although the amount of oil added did not

seem to be significant. Sample U5, which is colored with iron oxide, had the greatest loss of gloss, but other samples of black *urushi* and laccol with oil showed losses of gloss that were nearly as great.

Autofluorescence

In 2009, one of the authors carried out a study of the autofluorescence of Asian lacquer (Webb, 2011). In an extensive survey of lacquer objects at the Royal Ontario Museum and in the author's personal collection, it was observed that Asian lacquer always exhibited autofluorescence to a certain degree. Samples of new lacquer were also observed before and after exposure to light, but that study did not compare the fluorescence exhibited by different lacquer formulae or the relationship between autofluorescence and the extent of light exposure.

The creation of the sample boards for the current study provided an opportunity to learn more about autofluorescence. In the first experiment, two lacquer samples were exposed to light at 30-minute increments for a total of 12 hours. To achieve this, the two sample boards were covered with a grid of aluminum foil and Mylar with 24 windows, each 1 cm². All but one of these windows was then covered with aluminum foil. Exposure commenced, with the lamp run at 0.33 W m^{-2} , a black panel temperature of 50°C, chamber temp of 50°C and RH of 50%. After a 30-minute exposure, a new window was opened and this procedure was repeated over the course of 12 hours until all 24 windows were open. The sample boards

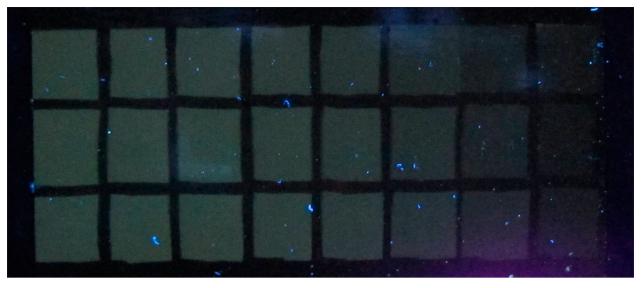


Figure 9 Black *urushi* with oil added (sample U4), observed under ultraviolet light after 12 hours light exposure in 30-minute increments at 0.33 W m⁻². Exposure increases from top left to bottom right.

for two of the lacquers, the *urushi*-based U4 and laccol-based L2, which had the same ratio of anacard lacquer to oil (25–68%) are shown in Figs. 9 and 10, respectively, photographed under ultraviolet (UV) light after 12 hours light exposure in 30-minute increments at 0.33 W m⁻².

Both the *urushi* and the laccol boards exhibited autofluorescence after as little as 30 minutes exposure to light. The intensity of the autofluorescence increased with the length of exposure to light until, after about six hours, the level of autofluorescence observed seemed to remain stable.

The longer-term light exposure experiments indicated a pattern of physical changes, which can be seen in Figs. 11 and 12. For several of the samples, the autofluorescence increased during the early stages of exposure but decreased after the first week. Although the transparent laccol and *urushi* samples showed the greatest autofluorescence, even these samples showed a reduction in intensity by the fourth week. Sample L5, the ground layer of which contained very high amount of tung oil, showed blue fluorescence at the unexposed edges and on the section exposed to light for only one week. This florescence disappeared with subsequent light exposure (Fig. 12). Sample U5, the Chinese *urushi* with iron oxide pigment did not fluoresce, which was expected as *bengara urushi* contains a high iron content and as light erodes the lacquer polymer the iron serves to quench any florescence.

These results help to explain previous conflicting observations regarding the fluorescence of Asian lacquer. In their book on furniture conservation Rivers and Umney included a photograph of a Japanese cabinet that indicated that excess light exposure reduced the autofluorescence of Asian lacquer (Rivers

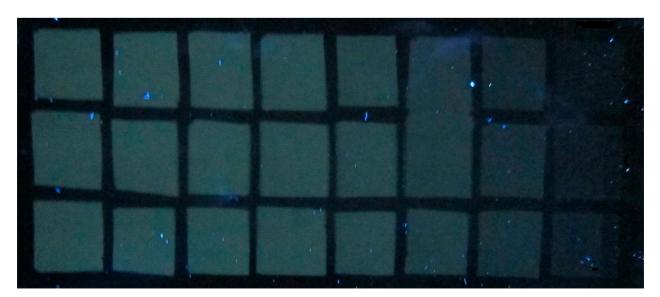


Figure 10 Black laccol with oil added (sample L2), observed under ultraviolet light after 12 hours light exposure in 30-minute increments at 0.33 W m⁻². Exposure increases from top left to bottom right.

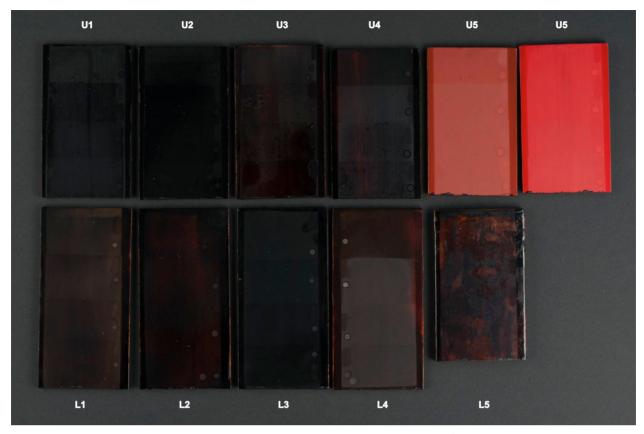


Figure 11 The sample boards imaged with visible light after light exposure at 0.5 W m⁻² for one to four weeks.

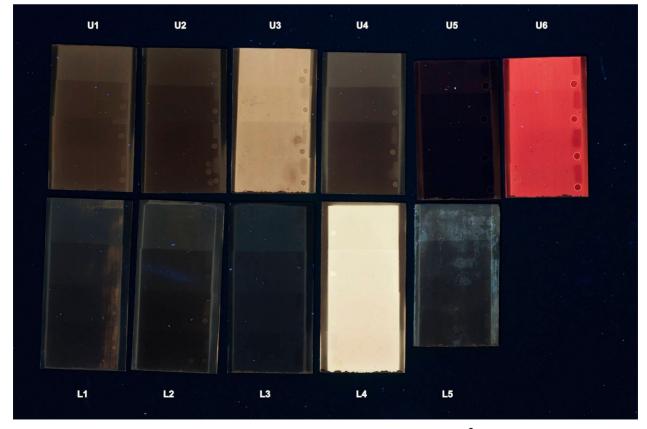


Figure 12 The sample boards imaged under ultraviolet light after light exposure at 0.5 W m^{-2} for one to four weeks. The amount of autofluorescence varies with time and with the formula of the lacquer sample.

& Umney, 2003). This behavior can now be better understood and defined because this research demonstrates that autofluorescence first increases then decreases. This research has not investigated the chemical or physical changes that may account for this phenomenon, but it may be that a secondary reaction occurs with ongoing exposure or that continued oxidation results in the destruction of the fluorophor.

Conclusions

The hypothesis that *urushi* has superior aging characteristics to laccol is not consistent with the results of this study. It has been shown that while *urushi* and laccol have some similar characteristics, the additives that they contain seem to have a greater effect on the aging characteristics than the type of lacquer.

There are a number of similarities between laccol and urushi formulae. Both show a range in pH on aging, but pH does not increase with time in either type of lacquer. The transparent formula without added oil has the lowest pH, which could indicate greater degradation of the lacquer. However, if gloss is used as a measure of degradation the two transparent anacards without added oil fare best. Oil does change the properties of either *urushi* or laccol and no clear patterns correlating the amount of added oil to the extent of deterioration were identified in this study. Future studies that control the amount of oil more precisely might find a relationship between oil content and changes in physical characteristics. The pigments used in a lacquer formulation, particularly those that are iron-based, appear to be very important and should be studied more closely.

The long process of THM-Py-GC–MS analysis and researching the use of the materials has paid off in the reproduction of more accurate Chinese export lacquer replica sample boards. As future research projects are carried out using these resources, conservators will hopefully be able to determine the behavior and aging characteristics of Asian lacquer objects according to the time and place of their manufacture. Conservation treatment, storage and display recommendations may, therefore, benefit from being specific to the objects' origin.

Recommendations for future research

Asian lacquer samples for experiments must include *urushi*, laccol, and *thitsi* as there are physical and chemical differences. Because the experiments described here also demonstrated that other ingredients are equally important to the behavior, consideration should also be given to the major additives used in the production of a lacquer.

The following formulae are suggested for future research. As each sample board differs by one ingredient, it should prove easier to determine which ingredient is influencing behavior. The entire set should contain identical ground materials while using the same anacard as the top test coating. This proposed set of 15 panels would provide a good general coverage of Asian lacquer types and the major ingredients commonly added.

- 1. Processed transparent lacquers: *urushi* (U), laccol (L), and *thitsi* (T) with no additives
- 2. U, L, and T with 15% oil added
- 3. U, L, and T with 15% oil and cinnabar pigment
- 4. U, L, and T with 15% oil darkened with iron filings5. U, L, and T with 15% oil darkened with iron filings
- and cedar oil 15%

(For thitsi add pine resin.)

Material and supplier

Finnish 3 mm thick, six-layer birch plywood: Lee Valley Tools Ltd, PO Box 1780, Ogdensburg, NY 13669-6780, USA.

References

- Chen, Z. & Shang, Z. 2002. Ben cao shi yi: ji shi (A supplement to Materia Medica). Hefei: Anhui ke xue ji shu chu ban she.
- Feller, R.L. 1994. Accelerated Aging: Photochemical and Thermal Aspects. Marina del Rey: Getty Conservation Institute.
- Heginbotham, A., Chang, J., Khanjian, H., & Schilling, M.R. 2016. Some Observations on the Composition of Chinese Lacquer. *Studies in Conservation* (special supplement) 61 (3).
- Heginbotham, A., Khanjian, H., Rivenc, R., & Schilling, M.R. 2008. A Procedure for the Efficient and Simultaneous Analysis of Asian and European Lacquers in Furniture of Mixed Origin. In: J. Bridgland, ed. ICOM Committee for Conservation, 15th Triennial Meeting New Delhi Preprints. New Delhi: Allied Publishers, vol. II, pp. 608–16.
- Institute of History and Philology. 1962. *Ming shi lu*. Nan'gang: Institute of History and Philology.
- Keneghan, B. 2011. Developing a Methodology for the Artificial Ageing of Urushi and a Preliminary Examination of Urushibased Conservation Options. In: S. Rivers, R. Faulkner & B. Pretzel, eds. East Asian Lacquer: Material Culture, Science and Conservation. London: Archetype, pp. 51–9.
- Kenjo, T. 1977. Interaction of Japanese Lacquer and Drying Oils. Science for Conservation, 16: 12–6 [in Japanese].
- McSharry, C. 2009. Conserving Tangible and Intangible Cultural Heritage: Cleaning Degraded East Asian Lacquer. PhD Thesis, Department of Chemistry, Imperial College, London.
- Ogawa, T., Arai, K., & Osawa, S. 1998. Light Stability of Oriental Lacquer Films Irradiated by a Fluorescent Lamp. Journal of Environmental Degradation, 6(1): 59–65.
- Rivers, S. & Umney, N. 2003. *The Conservation of Furniture*. Oxford: Butterworth Heinemann.
- Schellmann, N. & Rivers, S. 2005. Aqueous Cleaning of Photodegraded Oriental Lacquers – A Preliminary Examination of the Effect of pH and Ionic Concentration on Gloss and Colour. Zeitschrift für Kunsttechnologie und Konservierung, 19(2): 369–76.
- Takahashi, S., Tsukagoshi, M., Sato, T., Kitahara, Y., & Fujii, T. 2013. Thermogravimetry of the Thermal Degradation of Japanese Lacquer (*urushi*) Films. *Journal of Thermal Analysis* and Calorimetry, 111(1): 685–8.
- Thei, J. 2011. Artificial Ageing of Japanese Lacquerware and Comparison of Conservation Treatments for Photodegraded Japanese Lacquer Surfaces. PhD Thesis, Department of Chemistry, Imperial College, London.
- Webb, M. 2011. The Autofluorescence of Asian Lacquer. In: S. Rivers, R. Faulkner, & B. Pretzel, eds. *East Asian Lacquer: Material Culture, Science and Conservation.* London: Archetype, pp. 148–58.
- Yamashita, Y. & Rivers, S. 2011. Light-Induced Deterioration of Urushi, Maki-e and Nashiji Decoration. In: S. Rivers, R. Faulkner, & B. Pretzel, eds. East Asian Lacquer: Material Culture, Science and Conservation. London: Archetype, pp. 208–16.