New advances in understanding the curing, ageing, and photo-aging processes of blended Thitsiol/Urushiol Asian lacquers by THM-GC/MS and other techniques

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Introduction

Asian lacquer is a durable and beautiful coating material which has been used in Eastern Asia countries for thousands of years [1]. Nowadays, numerous western museums host a large number of precious Asian lacquered objects, often made by using a blend of the less expensive thitsi-type lacquer and urushi-type one [1,2]. In this work, for the first time, a blend of thitsi and urushi in three different percentage concentrations has been characterized and monitored during the curing, natural, and artificial ageing processes and a correlation with pure thitsi and urushi has been found. The using of physical and chemical techniques, such as Digital Microscopy in the first case and Fourier Transform Infrared Spectroscopy and Pyrolysis Gas Chromatography/Mass Spectrometry in the second one, allowed to describe the degradation process in all its aspects. This includes the formation of micro-cracks on the surface of the material strictly dependent on the formation of oxidation products in the chemical composition.

Materials

Material type selection

- Thitsi (Royal Forest Department of Thailand, Bangkok, Thailand)
- Urushi (Kremer, Germany)
- Essential Oil (Gurjun Balsam, Mystic Moments, Hampshire, U.K.)

Asian lacquer-models preparation

Application on glass-slides as 70 µm lacquer-film of

- Thitsi pure
- Thitsi filtered
- Thitsi filtered + 10% essential oil
- Urushi pure
- Urushi+Thitsi filtered (1:1)
- Urushi+Thitsi filtered (1:4)
- Urushi+Thitsi filtered + 10% essential oil (1:1)

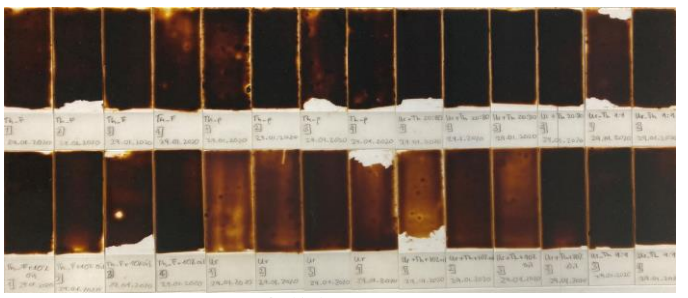


Figure 1: Asian lacquer-models as thin films

Curing Process

- Curing process in a climate chamber at 20 °C and 80 % rH
- Curing time: 8 weeks except for the pure urushi, which took 1 week

Daylight ageing

Daylight accelerated ageing chamber: UVACUBE SOL 500 RF2 (Dr. 2 Hönle, Germany) (460 W/m nominal irradiance) equipped with a filter glass H1, which provides radiation with wavelengths from 320 nm, thus allowing sun-glass filtered simulation.

- Ageing time: 31 days.

Instrument & Stoftwares

Digital Microscopy

Keyence VHX-6000 (RZ 100x-1000x objective - VH-Z100R) equipped with a LCD monitor and a CMOS camera (virtual pixels: 1600 (H) x 1200 (V)).

Fourier Transform Infrared Spectroscopy

Lumos (Bruker), germanium crystal (Ge) (n= 5.7), MCT detector, (128 scans, 4cm^{-1} resolution). Opus 8®

Thermally Assisted Hydrolysis and Methylation of Pyrolysis - Gas Chromatography / Mass Spectrometry

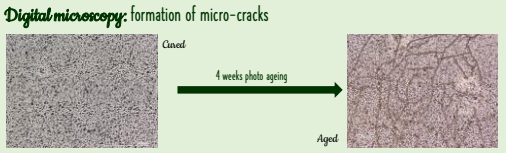
Pyrolyzer PY-2020id (Frontier Lab)with GCMS-QP2010 Plus(Shimadzu); column SLB-5ms (Supelco); GCMS Realtime

- Pyrolysis (Py) T 500 °C. Interface T 250 °C; injector T 280 °C. Reagent: 2 µL tetramethylammonium hydroxyde (TMAH) (25 wt% aqueous solution) (Sigma Aldrich).
- Solvent cut time 5 min, T ramp from 40 °C (2 min) to 300 °C by 6 °C/min, held for 20 minutes; He glas flow 1 mL/min; split ratio 1:50; MS interface and ion source at 280 and 200 °C, respectively; EI at 70 eV; scans from 50 to 750 m/z.

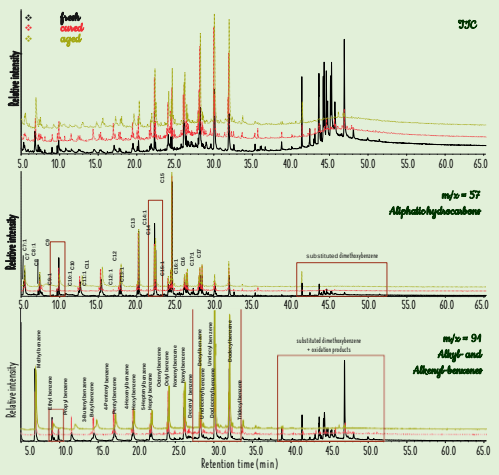
Results

Thitsi

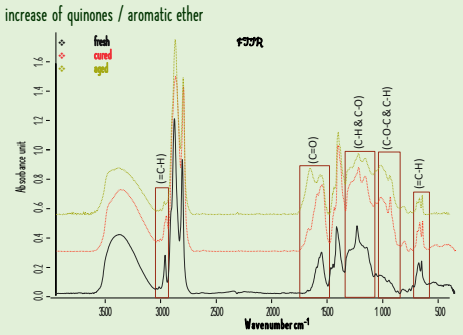
- **Digital microscopy:** formation of micro-cracks



- **THM-GC/MS:** decrease of C9:1 and C9, C14:1 and C14, substituted dimethoxybenzenes, alkenyl- and ethyl benzenes, increase of dodecyl benzenes and oxidation products

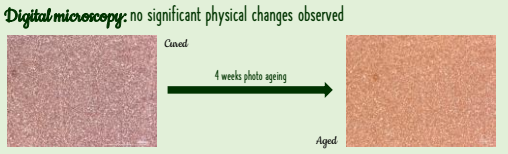


- **FTIR:** decrease of monomer cathecol / unsaturated side chains, aromatic displacement, increase of quinones / aromatic ether

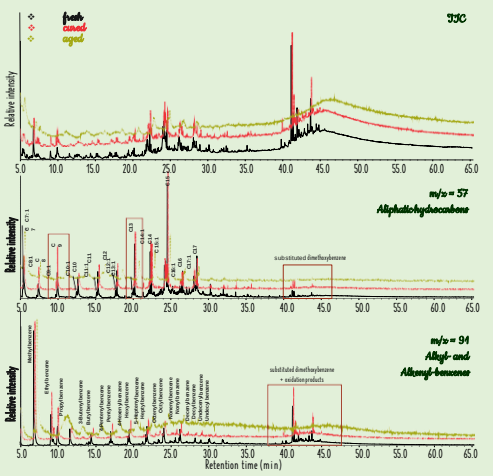


Urushi

- **Digital microscopy:** no significant physical changes observed



- **THM-GC/MS:** decrease of C9:1 and C9, C13:1 and C13, substituted dimethoxybenzenes, alkenyl- and ethyl benzenes, increase of dodecyl benzenes and oxidation products



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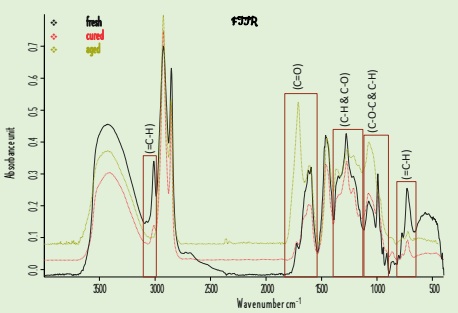
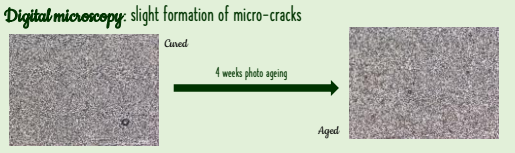


Thitsi+Urushi

- **Digital microscopy:** slight formation of micro-cracks



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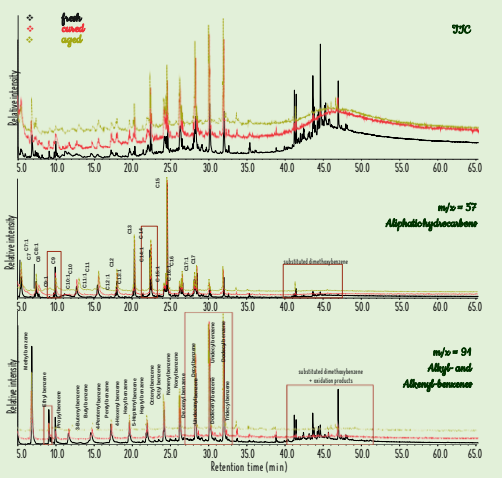

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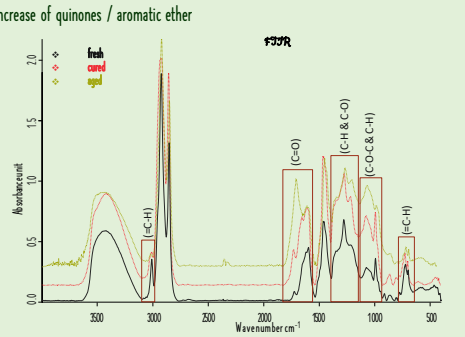

Conclusion & Outlooks

- This research suggested a successful analytical approach to better characterize blended *thitsiol/urushiol* in addition to pure thitsi and urushi as Asian lacquers, but also to study their curing, ageing, and photo-ageing processes.
- The chemical composition of the three lacquer-types has been investigated with a powerful analytical method such as THM-GC/MS, and together with FTIR it has been possible to study their chemical changes from the curing to the final artificial accelerated daylight ageing.
- Characteristic chromatographic markers has been detected and correlated with the chemical composition of each of the lacquers investigated as well as with their oxidative and aged state. New markers of oxidative products have been found.
- Physical changes such as the formation of fine micro-cracks on the material surface, during and after daylight ageing, has been visualized with digital micro-optical inspection. Micro-cracks were predominant in thitsi and in the blended *thitsiol/urushiol*.
- Further research is still ongoing to better understand the exact chemical processes involved in the ageing of blended *thitsiol/urushiol*, also including the investigation of cultural heritage lacquer objects.

References

[1] Le Hô, A.-S.; Regert, M.; Marescot, O.; Duhamel, C.; Langlois, J.; Miyakoshi, T.; Genty, C.; Sablier, M. *Analytica Chimica Acta*, **2012**, 710, 9-16

[2] Honda, T.; Ma, X.; Lu, R.; Kanamori, D.; Miyakoshi, T. *Journal of Applied Polymer Science*, **2011**, 121, 2734-2742

Aknowledgments

Many thanks to Jonas Veenhoven (Royal Institute for Cultural Heritage (KIK-IRPA), Brussel, Belgium) for kindly providing the thitsi lacquer.